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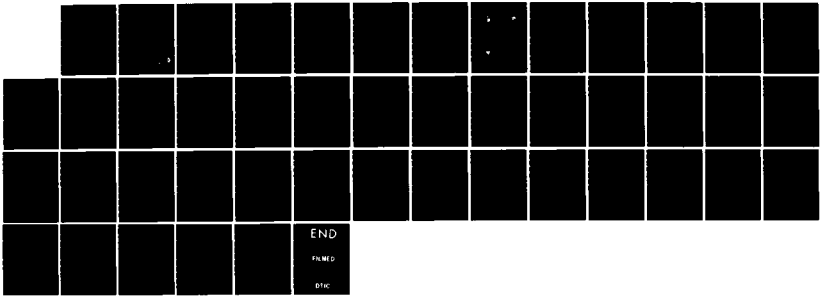

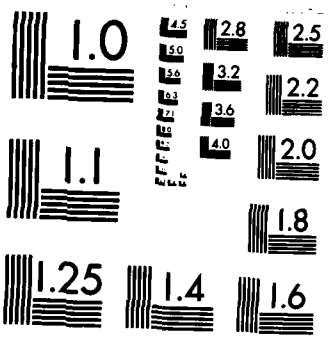

SYNTHESIS OF ENERGETIC MATERIALS
ANNUAL PROGRESS REPORT FOR THE OFFICE OF NAVAL RESEARCH

WORK REQUESTS N0001484WR24121 AND
N001485WR24088
PROJECT RR024-02-01/02-0D

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March 1985

Research and Technology Department

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The synthesis of polyformals from several nitro- and fluorodiols was investigated. Linear, difunctional polyformals were obtained from 3,3,5,7,7-pentanitro-5-azanonanediol, 3,5,5,7-tetranitro-3,7-diazanonanediol, 2,2,3,3,4,4-hexa fluoropentanediol, and 2,2,3,3,4,4,5,5-octafluorohexanediol. Procedures are given to prepare stable gumstocks from the first 3 of these, using FEFO as plasticizer. The fourth polymer was only partially miscible with FEFO.

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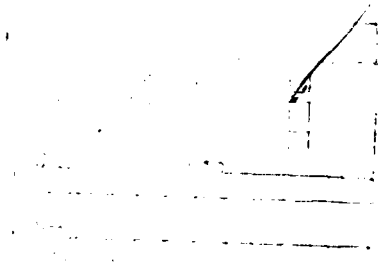
20. Abstract

Efforts toward the synthesis of polyazabicyclooctanes and polyazaoxabicyclononanes were continued. An acyclic model compound for the latter system was synthesized and found to be marginally stable. Various approaches to the synthesis of azacyclooctadienes as precursors to bicyclononanes were investigated. A study of the chemistry of the 2,6-diazabicyclooctane ring system was initiated. Condensation reactions of 2,3-disubstituted and 2,3,5,6-tetrasubstituted 1,4-dinitropiperazines with methylene diamine derivatives were investigated in efforts to prepare linear polycyclic nitramines. During this work, the first example of a 1,2-dinitraminoolefin was prepared. A new oxidizer of exceptionally high oxygen content, 2,3,5,6-tetranitrato-1,4-dinitropiperazine, was prepared but was found to decompose slowly at room temperature. Originator Supplied Keywords include)



CONTENTS

ILLUSTRATIONS

SYNTHESIS OF ENERGETIC MATERIALS

INTRODUCTION

The work described in this report was carried out during 1984 under the sponsorship of the Office of Naval Research, Code 432P (Dr. R. S. Miller). The effort consisted of two separate tasks which will be discussed in turn: (1) synthesis of energetic monomers and polymers, and (2) synthesis of polycyclic and adamantoid nitramines. Both tasks were continuations of previous work, and pre-1984 results are reported in ref. 1. The principal objectives of the work are the synthesis of energetic (nitro) polymers with improved energy and physical properties, specifically polyformals derived from nitro substituted diols, and the synthesis of nitramines with high crystal density and energy-density greater than HMX.

ENERGETIC POLYMER AND MONOMER SYNTHESIS

In continuation of the previous work[1] under this task, the formation of hydroxy-terminated polyformals from selected nitro- and fluorodiols was investigated further.

It has been shown in the earlier work that 3,3,5,7,7-pentanitro-5-azanonanediol (1) on reaction with CH_2O/BF_3 etherate formed a mixture of linear and some cyclic polyformals, the former being hydroxy-terminated and thus cross-linkable with di/triisocyanates. These polymers were readily soluble in FEFO, and the FEFO solutions were readily cured with PAPI-135.

$$HOCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2OH \xrightarrow[BF_3 \cdot 2Et_2O]{CH_2O}$$

1

$$HOCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2O\{CH_2OCH_2CH_2C(NO_2)_2CH_2\overset{NO_2}{\underset{|}{N}}CH_2C(NO_2)_2CH_2CH_2O\}_xH$$

+ 12, 24, 36 ring cyclic formals

However, formation of bubbles thought to be due to residual formaldehyde was observed during the cure. During this year's effort a new sample of the polymer was prepared by the previous procedure,[1] except that a treatment of the crude polymer with hydrogen peroxide was added. FEFO solutions of this sample cured well without bubbling in several attempts, but produced a few bubbles in others. A larger quantity of the polymer was then prepared from 30g of the diol 1 by the modified procedure. The polymer yield was 25g ($M_n \approx$ 2800); based on the GPC (Fig. 1) and hydroxy group determinations, the cyclic formal content was estimated to be 8%. The curing of this polymer was studied in an effort to determine the cause of and alleviate the residual bubbling during cure. It was found that a good cure and void-free gumstocks could be obtained by the addition of <1% each of N-methyl-4-nitroaniline and N-phenyl-2-nitroaniline. These gumstocks had an excellent elongation and tear strength. About 20g of the polymer are available for further evaluation.

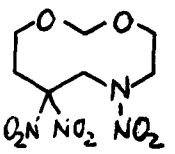
Some additional work was carried out on the synthesis of 1. The previously reported synthesis[1] of potassium 3,3-dinitropropanol was repeated on a 50g scale, and the initially obtained yields were confirmed. The conversion to 3,3-dinitropropyl acetate was improved and now gives a 75% yield. The remainder of the synthesis of 1 remains unchanged. About 30g of 1 was prepared for conversion to the polyformal.

$$O_2NCH_2CH_2CH_2ONO_2 \xrightarrow[\text{aq. MeOH}]{\text{KOH}} K\,C(NO_2)_2CH_2CH_2OH \quad (60\text{-}70\%)$$

$$\xrightarrow[\text{2. } CH_3COCl]{\text{1. } H_2SO_4} HC(NO_2)_2CH_2CH_2OAc \quad (75.5\%)$$

5g of pure diol 2 was prepared by the earlier[1] reported procedure, and the polymer formation with CH_2O/BF_3 etherate in sulfolane was studied. Even under the best conditions found there was still about 30% cyclic formal in the

$$\underset{\underset{2}{}}{HOCH_2CH_2\overset{\overset{NO_2}{|}}{N}CH_2C(NO_2)_2CH_2CH_2OH} \xrightarrow[BF_3]{CH_2O} \text{POLYFORMAL} +$$



product mixture. The GPC of this material is shown in Fig. 2. Unless more favorable conditions can be found, 2 is therefore of questionable utility as a monomer in the polyformal reaction. No further work is planned at present.

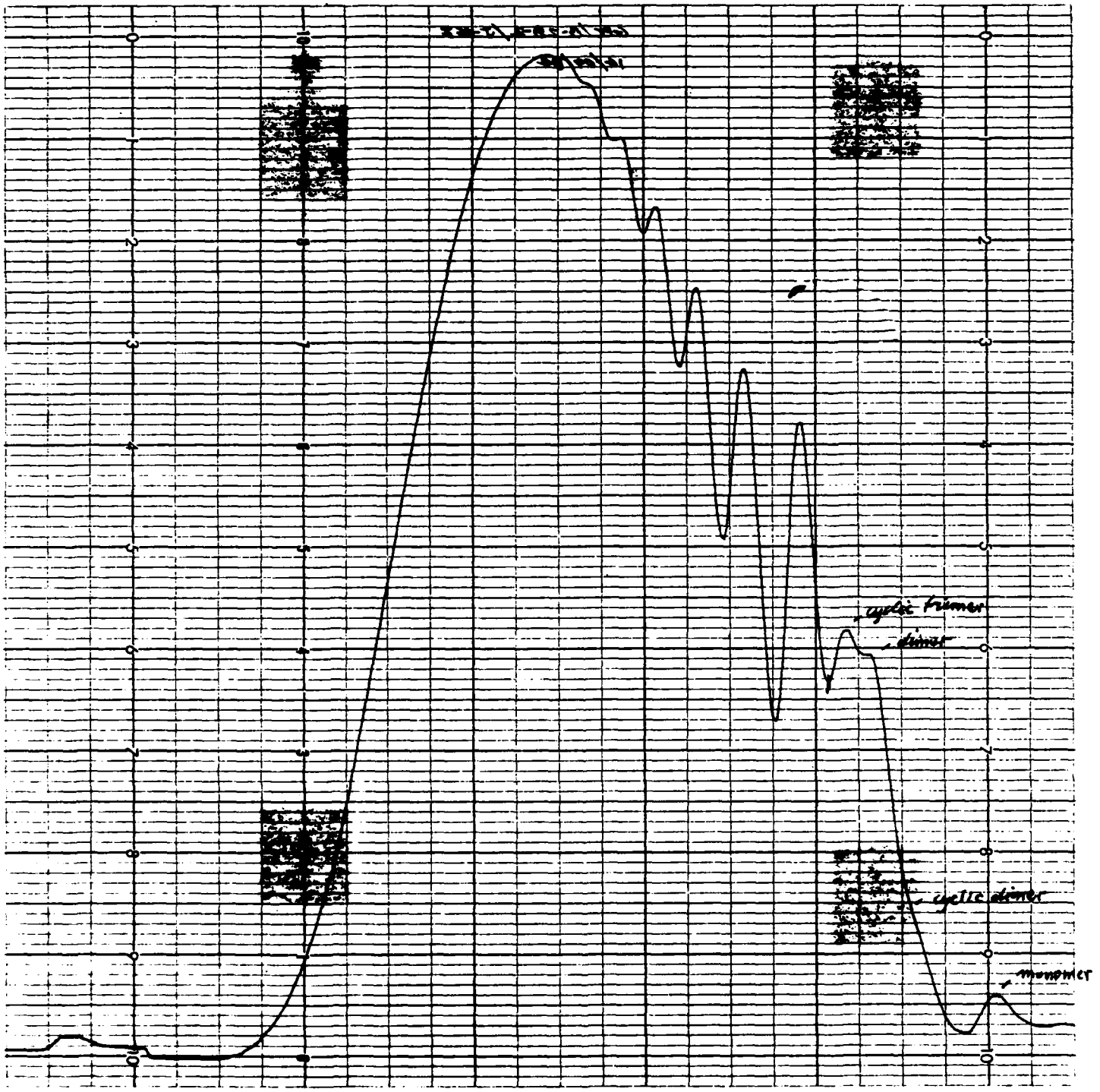


FIGURE 1. GPC OF POLYFORMAL OF 1 FROM MODIFIED PROCEDURE

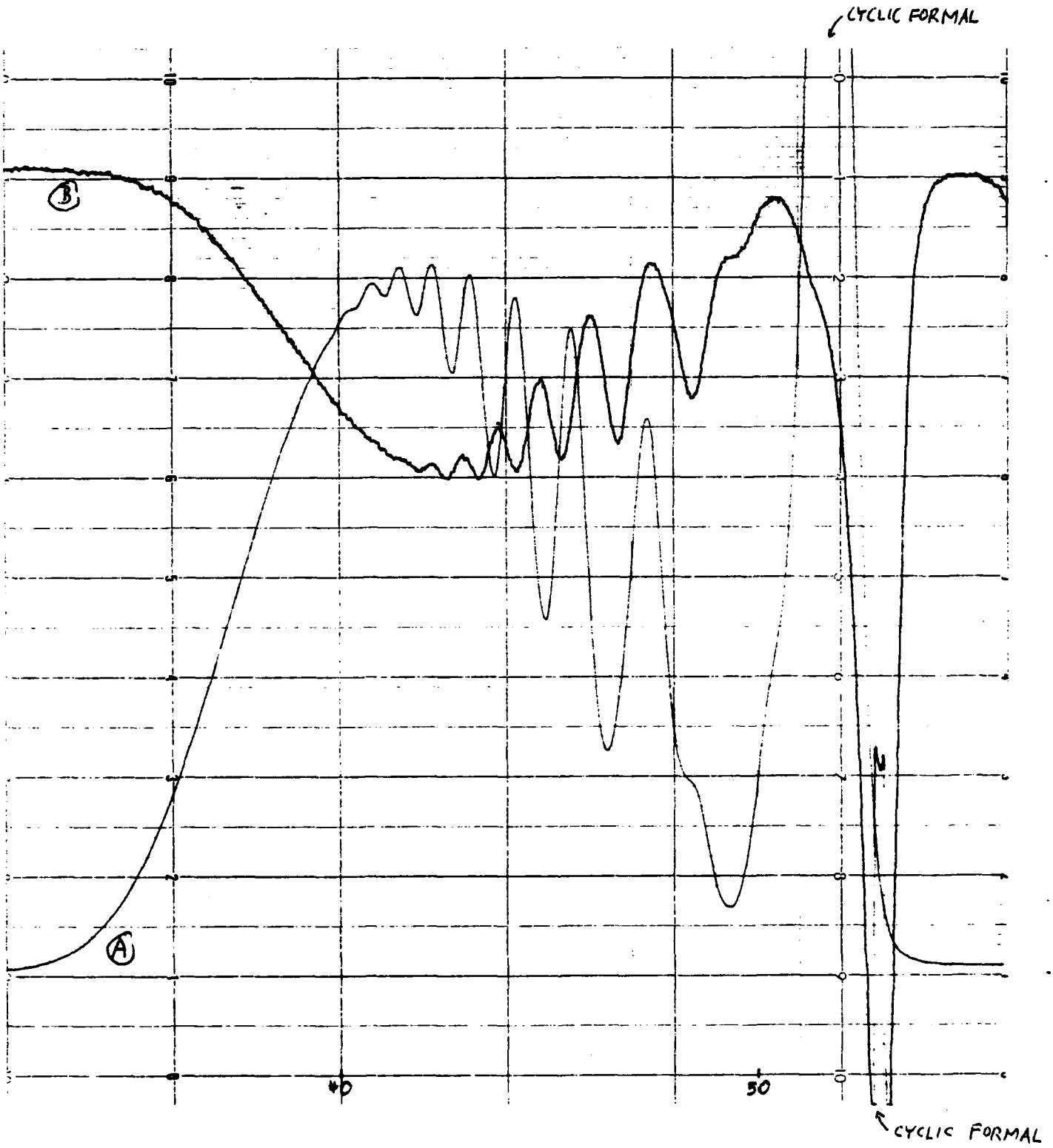


FIGURE 2. GPC OF POLYFORMAL OF 2; A: UV DETECTOR; B: RI DETECTOR

Diol 3 was synthesized recently to study the effects resulting from the exchange of nitramine for gem-dinitro groups and vice versa on the course of the reaction with formaldehyde and on the properties of the resulting polymer. Depending on the density, this polymer could be comparable in energy to that from 1. The synthetic approach to 3 is shown below:

$$NaCX_2H + CH_2O + H_2NCH_2C(=O)OEt \longrightarrow HCX_2CH_2NHCH_2COOEt$$

$$\xrightarrow{HNO_3} HCX_2CH_2\overset{X}{N}CH_2COOEt \xrightarrow[2.\ HNO_3]{1.\ H_2NCH_2COOEt} EtOOCCH_2\overset{X}{N}CH_2CX_2CH_2\overset{X}{N}CH_2COOEt$$

$$\xrightarrow[2.\ BH_3\text{-}THF]{1.\ HOAc/H^+} HOCH_2CH_2\overset{X}{N}CH_2CX_2CH_2\overset{X}{N}CH_2CH_2OH$$

3 $\qquad$ X = NO_2

Ten grams of 3 was prepared by this method. The pure diol melted at 95-7°C, about 25° lower than 1. A polyformal ($M_n \simeq 3000$) was prepared from 3 in about 90% yield by reaction with trioxane in sulfolane with BF_3 etherate as catalyst. The GPC (Fig. 3) and hydroxy group analysis indicated a cyclic formal content of only about 3%. Despite the lower melting point of 3, its polyformal was less soluble in FEFO than that from 1. However, a solution of 1 part of polyformal from 3 in 3 parts (w/w) of FEFO held at 60°C cured with PAPI-135/DBTDL to give a bubble-free gumstock which was stable to extended storage at room temperature (no phase separation). On the basis of these preliminary experiments it appears that the polyformal from 3 is more compatible with the gumstock components FEFO, PAPI-135, and DBTDL and is therefore more suitable as a binder component.

In previous work[1] investigation of polyformal formation from fluorodiols 4 and 5 was initiated. Diol 4 was obtained commercially; the 3M Company[2]

$$HOCH_2(CF_2)_nCH_2OH$$

4 : n = 3
5 : n = 4

provided an experimental sample of diol 5. The polyformals of these diols were of interest because of anticipated miscibility with energetic plasticizers such as FEFO, which are not compatible with the more highly fluorinated commercial fluoropolymers such as 3 M's FC 2202 polyether and L 4093 functionalized Fluorel.

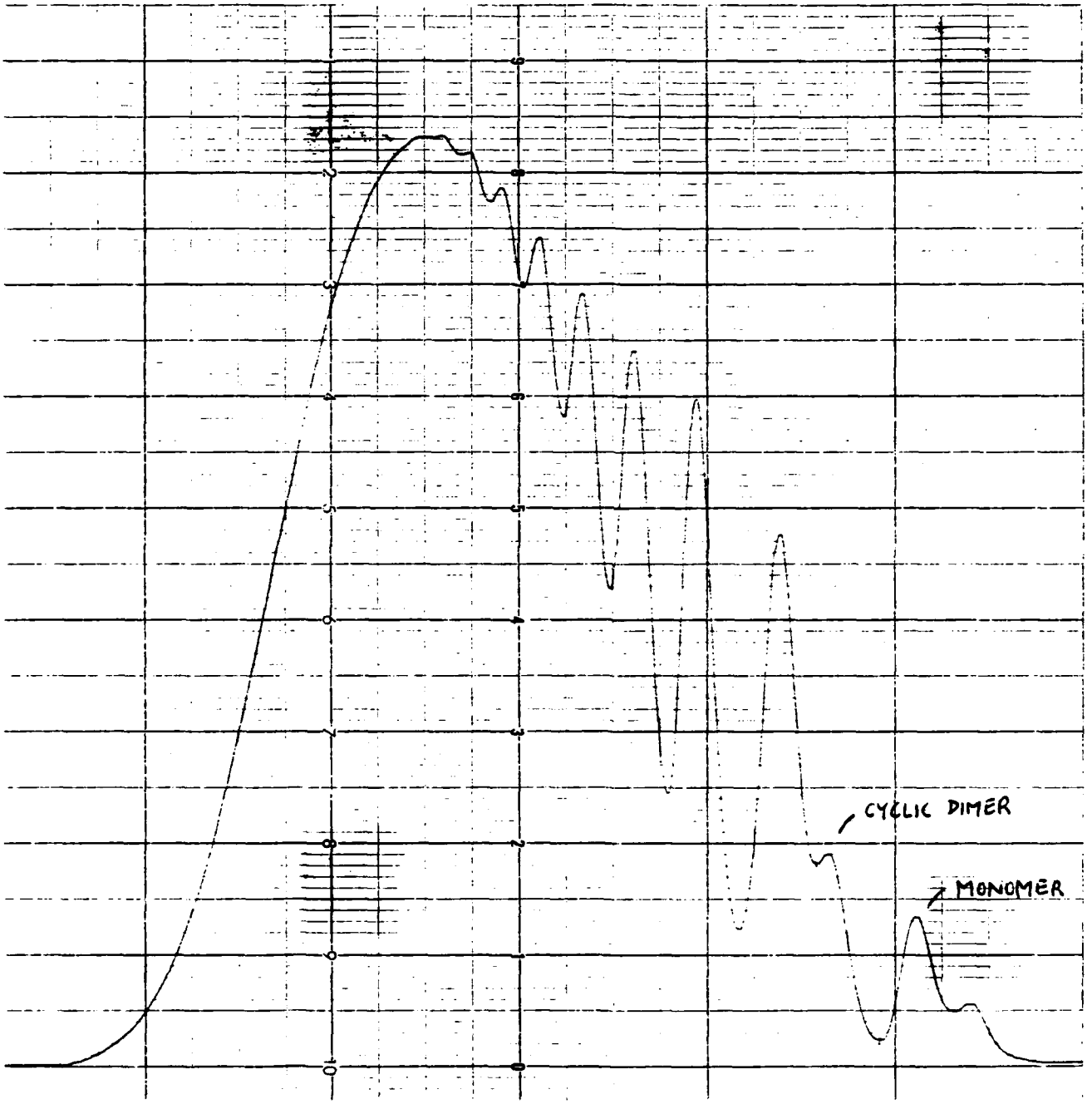
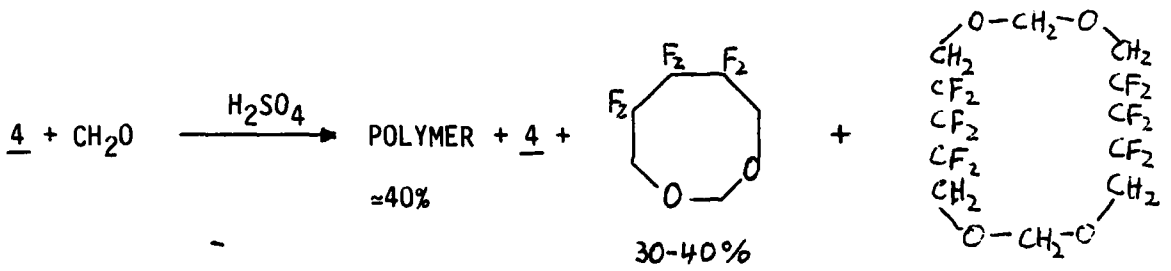


FIGURE 3. GPC OF POLYFORMAL OF 3

There are two reports in the literature of attempted preparations of polyformals of 4 and 5; in the case of 4, very low molecular weight polymers (m.w. 600-800) were obtained;[3] in the case of 5, the polymer was obtained from the cyclic formal, and the properties and m.w. were not determined.[4] In the work under this task, diol 4 was reacted with formaldehyde in approximately 85% sulfuric acid to give a mixture of polymer, unreacted monomer, and cyclic formals. The low molecular weight products were readily removed by heating



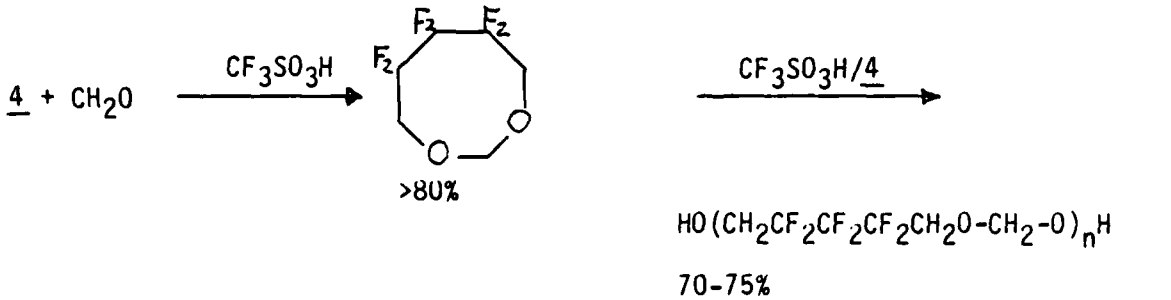
to 120°C in vacuo. The resulting polymers had molecular weights in the 3000-4000 range depending on the formaldehyde/monomer ratio. A larger scale run gave the material shown in Fig. 4 with the following characteristics:

OH equivalent weight: 2098 (includes about 5% of cyclic dimeric formal in the sample)

$\overline{M}_n$: 4046
Functionality ≈2

A gumstock prepared from a similar polymer of equivalent weight 1813 with FEFO as plasticizer (Pl:Po = 2:1) and PAPI-135/Dibutyltin dilaurate as curative was well cured after 2-3 days at 50°C and had a density of 1.59 g/cm^3. The properties of this gumstock demonstrate excellent miscibility and compatibility of the polymer with FEFO.

An improved synthesis for hexafluoropentanediol polyformal was developed which gives improved yields and excellent molecular weight control over the range M = 2,000 - 20,000. The method consists of the conversion of the diol to hexafluorodioxocane with formaldehyde/triflic acid (>80% yield) followed by triflic acid catalyzed polymerization of an appropriate mixture of diol and dioxocane to produce the desired molecular weight. The polymer yield is 70-75%. Fluorodiol not converted to polymer can be recovered and recycled.



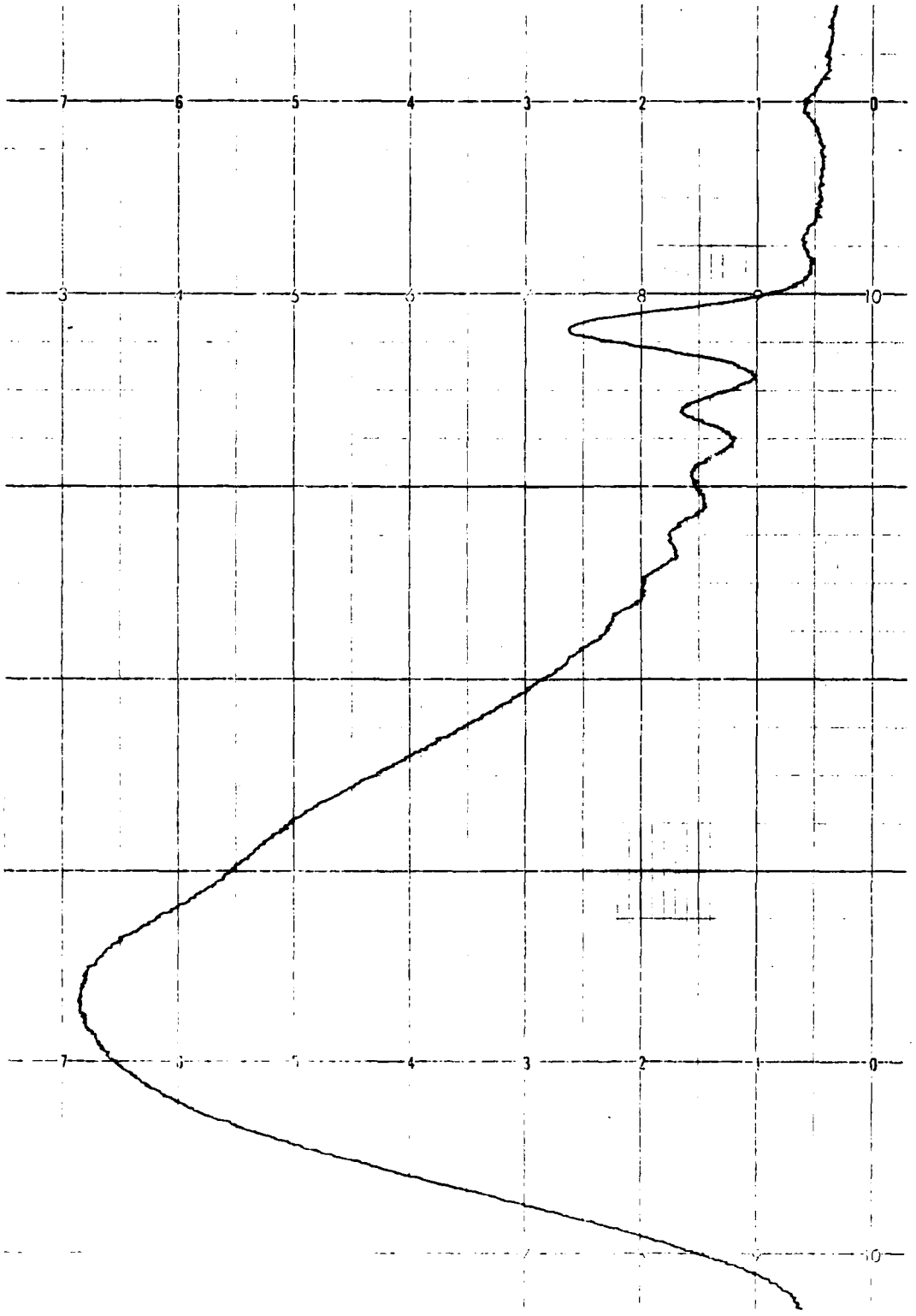
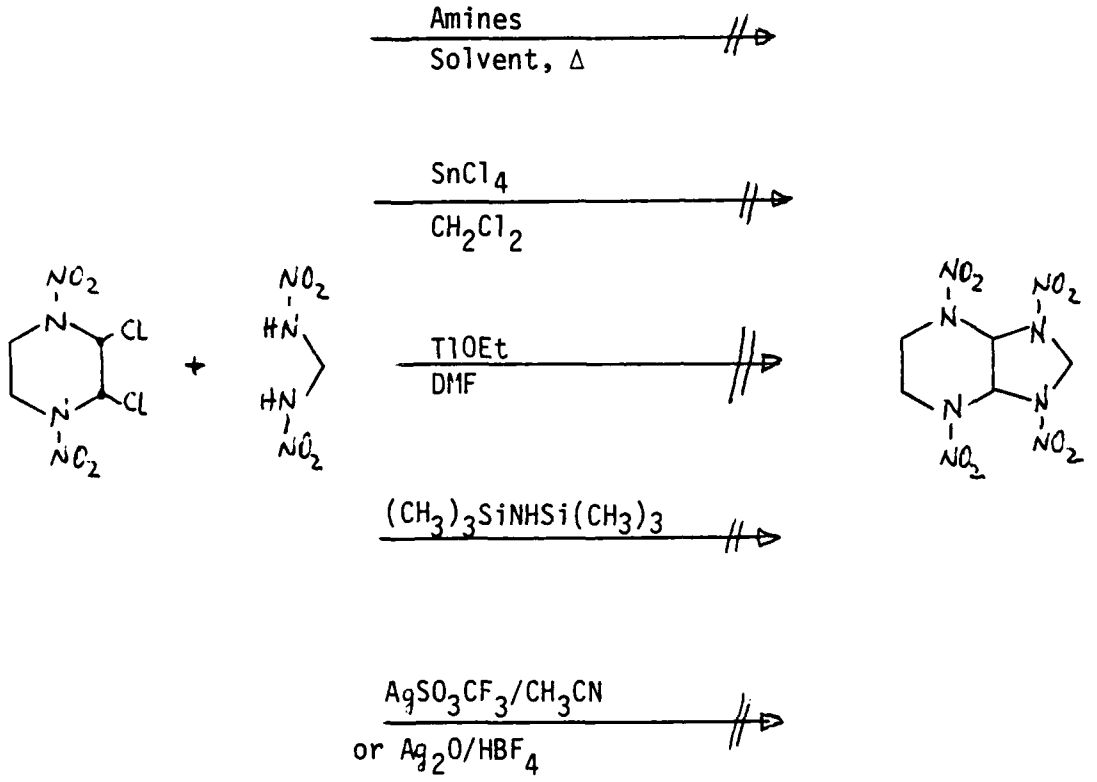
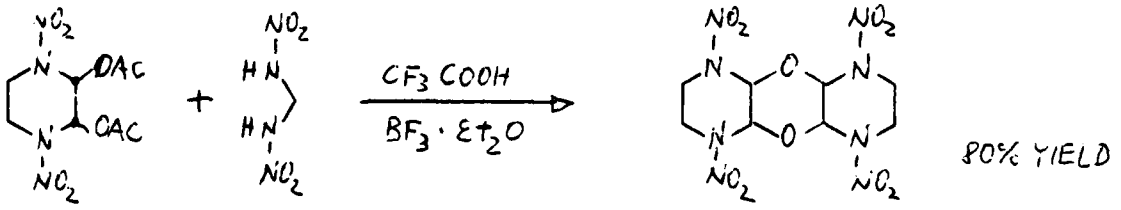


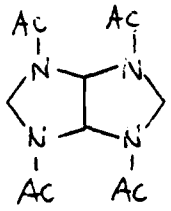
FIGURE 4. GPC OF POLYFORMAL OF $HOCH_2(CF_2)_3CH_2OH$; CYCLIC FORMALS ARE NOT COMPLETELY REMOVED

Although this ring system is not strained and both cis- and trans-isomers are formed with almost equal ease in the carbocyclic ring system, the reactions tried so far were not successful.



Reactions of 22c and 22d with NH_3, tert-butylamine, and urea also gave no isolable products. Under some conditions self-condensation products of 22 were obtained which were shown to be oxa-analogs of the desired polycyclic nitramines, an indication that such ring systems are stable.



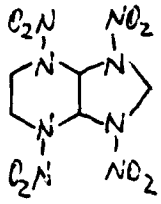


$\xrightarrow[0°/CH_3CN]{N_2O_5}$ Foamy polymeric solid; NMR shows that ring is destroyed.

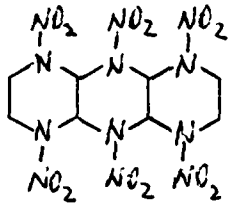
$\xrightarrow[-40°C]{HNO_3(100\%)/N_2O_5}$ Water soluble oils.

$\xrightarrow[2.\ NaNO_2]{1.\ BBr_3}$ NO_2 fumes. Water soluble products.

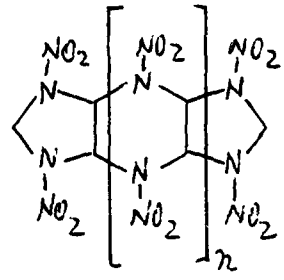
Other structures among linear polycyclic nitramines which are of interest to us are shown below. Exploration of synthetic approaches to these compounds has been a major part of the project effort during CY 1984.



ρ_0 (CALC'D) = 1.84



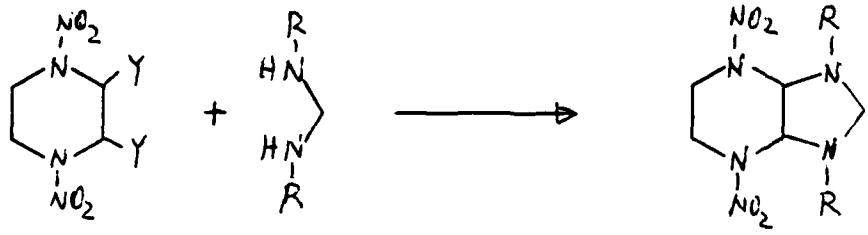
ρ_0 (CALC'D) = 1.83



$n = 1$: ρ_0 (CALC'D) = 1.95

$n = 2$: ρ_0 (CALC'D) = 1.96

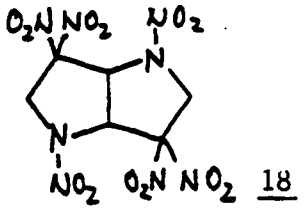
In the recent work, condensation reactions of 24 were explored as a first step which would lead to the [4,3] bicyclononane ring system:



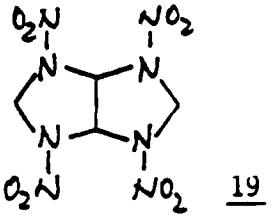
Y = OAc (22a), $CF_3\overset{O}{\overset{\|}{C}}O$ (22b),

Cl (22c), Br (22d)

Among the linear polycyclic nitramines whose synthesis we have pursued are the diaza- and tetrazabicyclooctanes 18 and 19. Some simple approaches

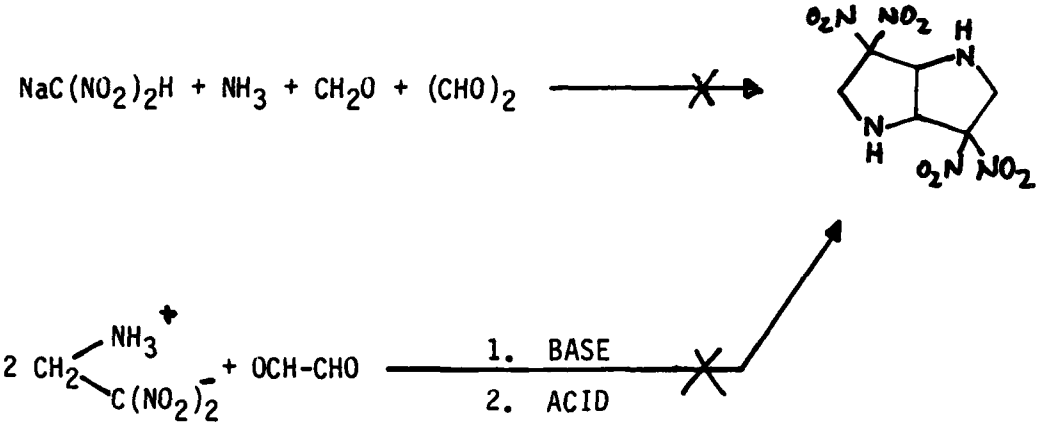


18

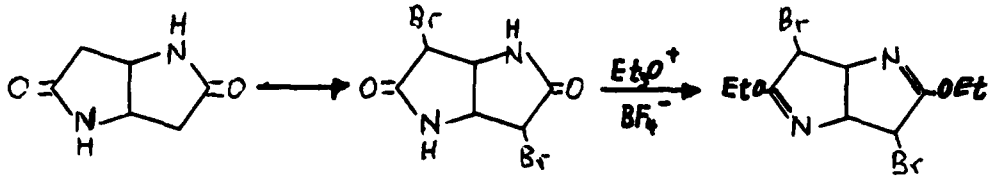


19

to the parent amine of 18 were tried and failed to give the expected product:



A more promising route starts with derivatives of the known dilactam 20. This compound can be brominated and alkylated to give 21. The chemistry of these diazabicyclooctanes is currently being investigated with a view toward synthesis of 18 and its dioxo derivative.

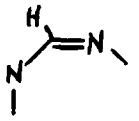


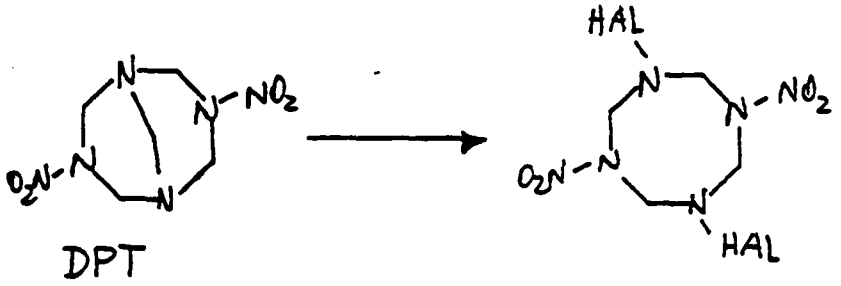
20 21

A few more attempts were made at the nitrolysis of the previously synthesized tetraacetyltetrazabicyclooctane to 19. Like all previous such attempts, they were unsuccessful.

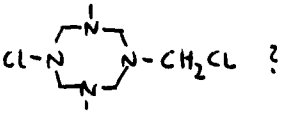
1. Br_2 1:1 OR EXCESS; DCE OR SULFOLANE;
   R.T. - 60°
   → RING DEGRADATION; NH_4Br

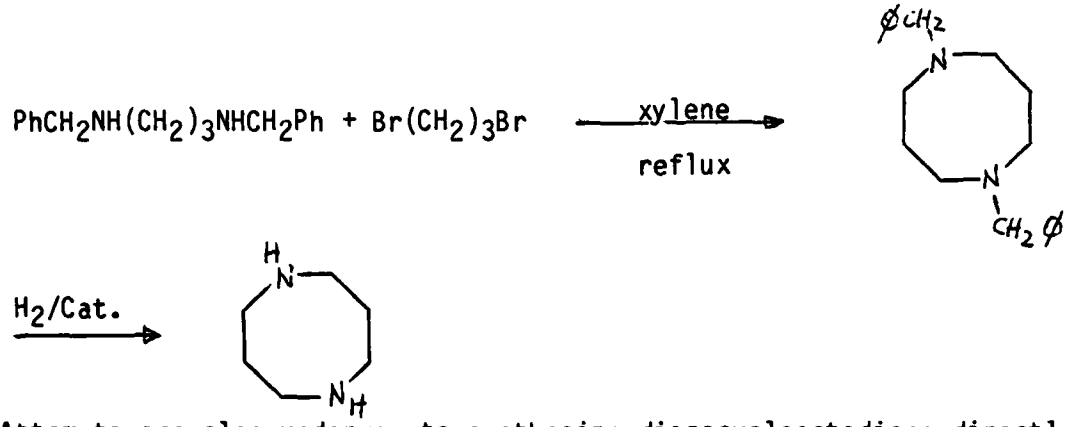
2. T-BUTYL HYPOCHLORITE 1:2; CH_2Cl_2;
   R.T., 24h
   → DAPT SALT + OIL; NMR EVIDENCE FOR



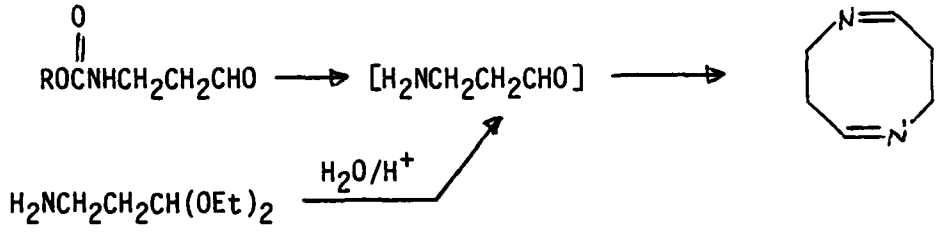


DPT

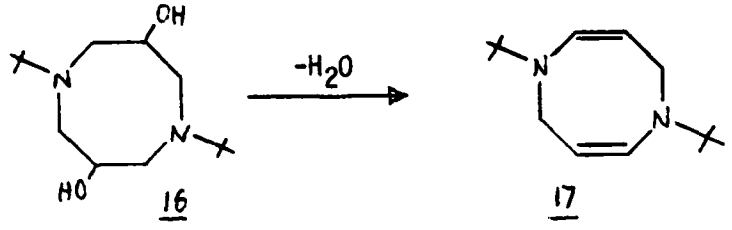
REAGENT/CONDITIONS	RESULT
BROMINE/SULFOLANE R.T. - 60°	ADDUCTS (?); DPT CAN BE REGENERATED
Br_2/SILVER ACETATE; MeOAc, R.T.	LITTLE REACTION
m-CHLOROPERBENZOIC ACID; MeOAc, R.T.	PRODUCT FORMS DPT + GAS ON STANDING; NMR SIMILAR TO BROMINE ADDUCTS
DITTO, 20h REFLUX	SMALL AMOUNT UNIDENTIFIED SOLID; DPT; MIXTURE OF SOLUBLE PRODUCTS
PCl_5/SULFOLANE, MeOAc; R.T.	ADDUCT FORMATION AND WATER-SOLUBLE PRODUCTS
CHLOROSUCCINIMIDE/DCE; REFLUX	NO REACTION
T-BUTYL HYPOCHLORITE/ SULFOLANE, MeOAc; 70°	PRODUCT MIXTURE WITH POSSIBLE H-C=N SIGNAL IN NMR
CHLORINE; MeOAc; R.T.	HYGROSCOPIC SOLID :  ?
Cl_2/NaOAc; MeOAc; R.T.	PRODUCT WITH STRONG  SIGNAL



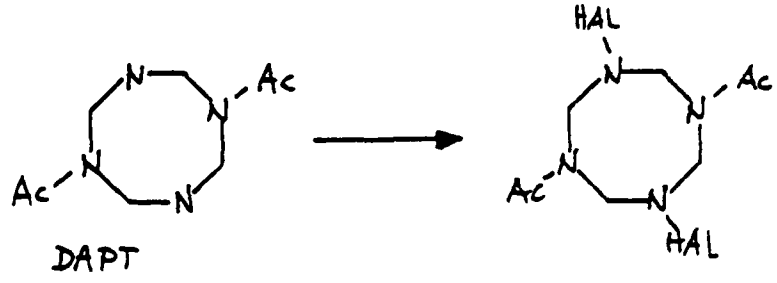
Attempts are also underway to synthesize diazacyclooctadiene directly by the two routes shown:

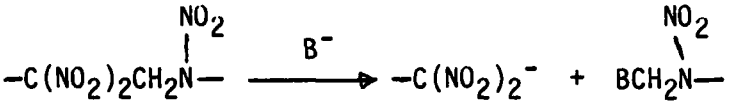


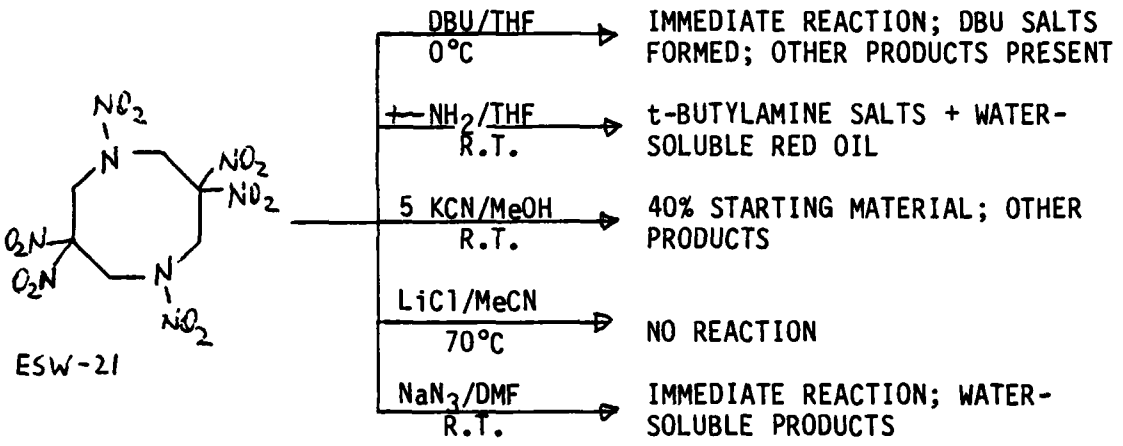
We have also prepared a quantity of the dihydroxydiazacyclooctane 16 by a known route and are studying its dehydration to the diene 17, another substrate of interest for transannular addition reactions.



Attempts have also been initiated to prepare compounds 15 by halogenolysis or similar reactions of DAPT and DPT. In these reactions, which are tabulated below, NMR evidence has been obtained for formation of the desired -N-CH=N- moiety, but pure products have not yet been isolated.

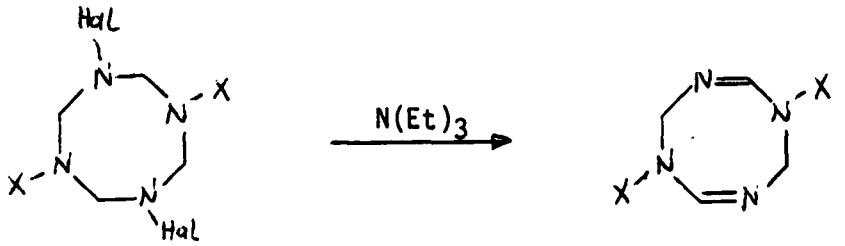






We plan to repeat some of these reactions at low temperature, if a suitable solvent can be found, in the hope that more tractable products will be formed.

Another possible route to 13 is elimination of HCl or HBr from N-haloamines such as 15. Such eliminations have been carried out with simple

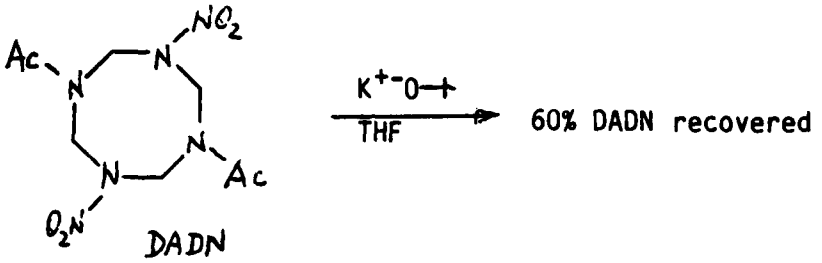


15

chloramines and occur quite readily. Since a milder base can be used for the first step, it may be possible to avoid the subsequent reactions which were observed with DMMD and HMX.

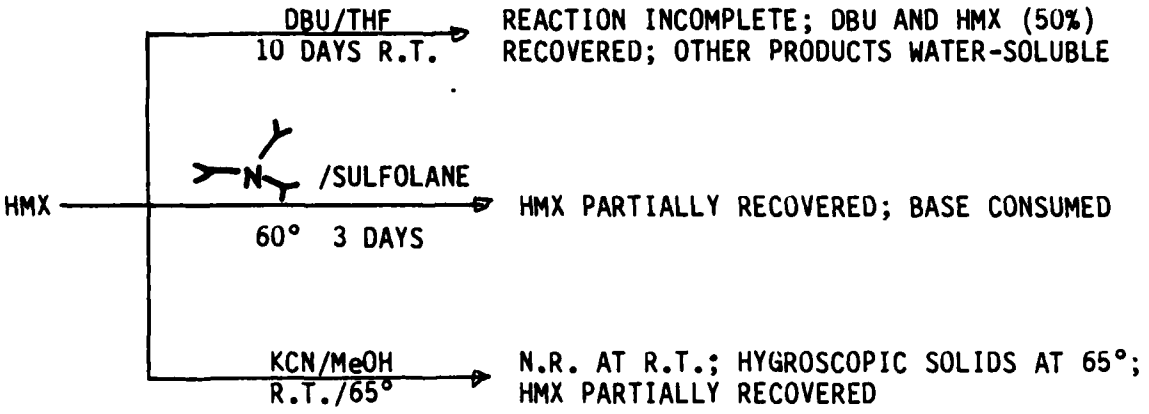
Again for the purpose of conducting model studies, the synthesis of 1,5-diazacyclooctane was initiated. This material will be chlorinated, and dehydrochlorination and transannular additions will be studied.

When HMX was reacted with one equivalent of potassium tert-butoxide, about 80% of it was recovered unchanged while the base had been consumed, again indicating multiple reactions. A similar result was obtained with DADN:



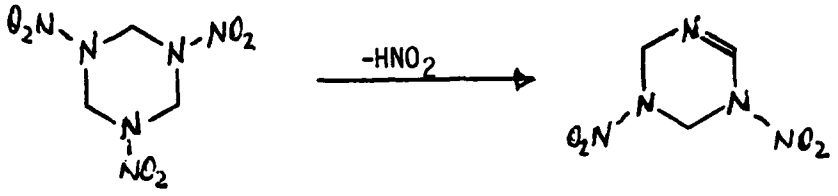
The above reactions were all quenched in D_2O; the recovered starting materials showed no deuterium incorporation by NMR.

HMX was also reacted with several other bases and nucleophiles; in all cases a similar reaction pattern was observed (i.e., consumption of base, partial recovery of HMX; water soluble products, if any). It appears from these results that nitrous acid elimination from a methylene dinitramine unit is not a feasible approach to structure 13.



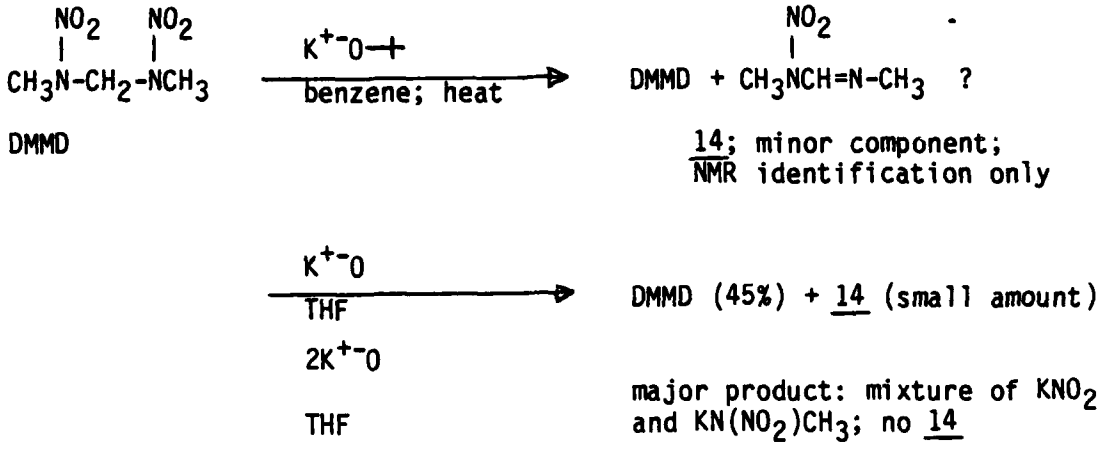
In contrast to the methylene dinitramines, 2,2-dinotroethyl nitramines such as ESW-21 were highly reactive with bases. A number of reactions which have been tried gave no isolable, well-defined products, however. In this case a possible complication is the reverse Mannich reaction which would lead to ring-opening and water-soluble dinitroalkane salts:

Since nitrous acid elimination from RDX had been reported earlier, [6] this reaction was studied with both acyclic and cyclic substrates to assess its

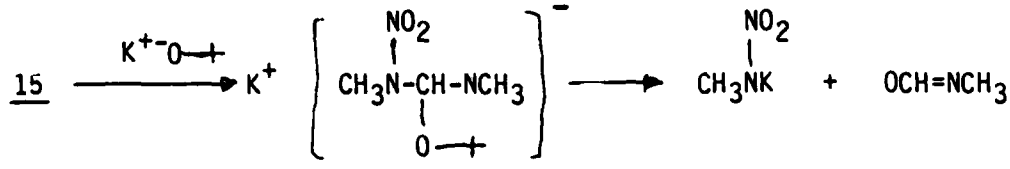


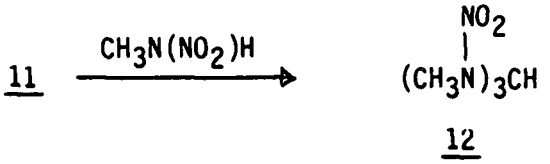
potential as a route to 13.

The reaction of DMMD with bases was studied as a simple model for the more complex reaction in a cyclic system. In view of Hoffsommer's results[6] it was surprising that DMMD did not react with sodium hydride in benzene, with butyl lithium in THF, or with lithium tetramethyl piperidide in THF. Reaction did occur, however, with potassium tert-butoxide:



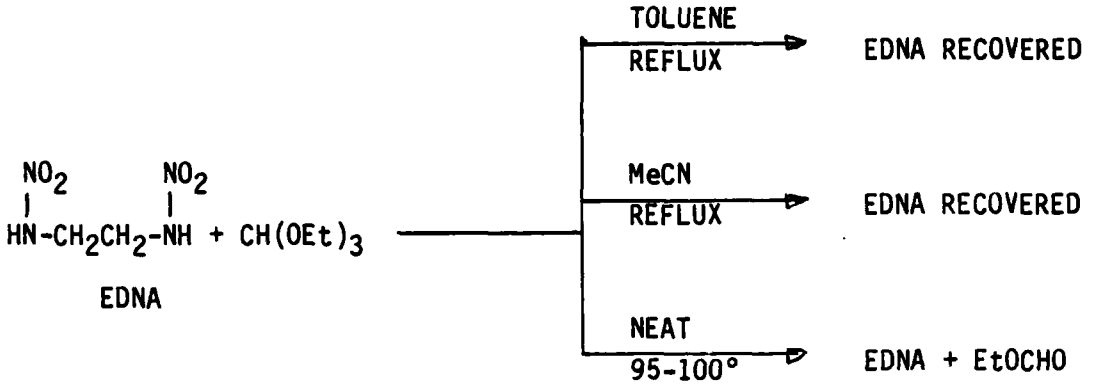
It appears that the desired reaction takes place but that 14 reacts more rapidly with base than the starting material. The nature of the second step is not known, but it could be a displacement reaction leading to the formation of potassium methyl nitramine, which was observed as a reaction product.



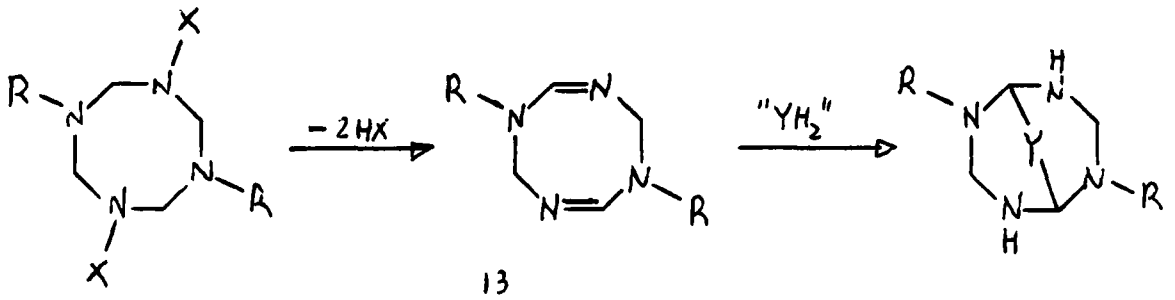


compound 8 should be stable also. The alkoxymethylene dinitramine structure of 11 should be stabilized by incorporation into the bicyclononane ring system.

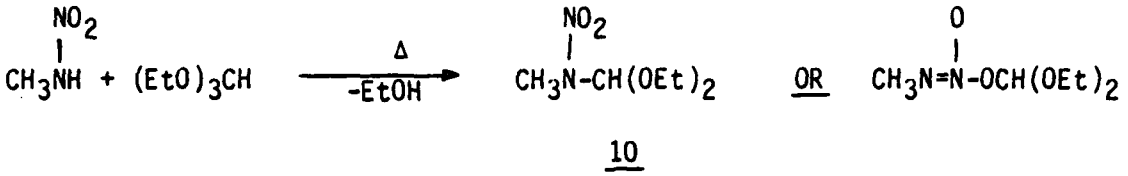
The reactions leading to 10 and 11 were also carried out with ethylene dinitramine instead of methyl nitramine. It was hoped that formation of the 5-membered ring would provide a strong driving force for these reactions. However, this was not the case, and the desired products were not obtained. We currently have no convincing explanation for this unexpected finding.



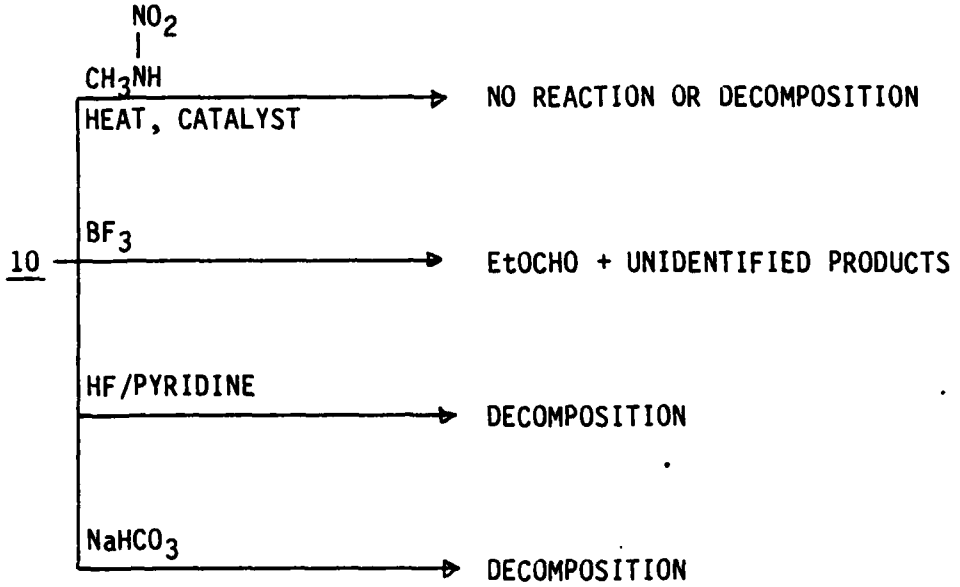
One synthetic approach to compounds 6 and 8 we decided to pursue involves the generation of the appropriate cyclooctadiene precursor and introduction of the hetero-atom bridge via a transannular addition reaction:



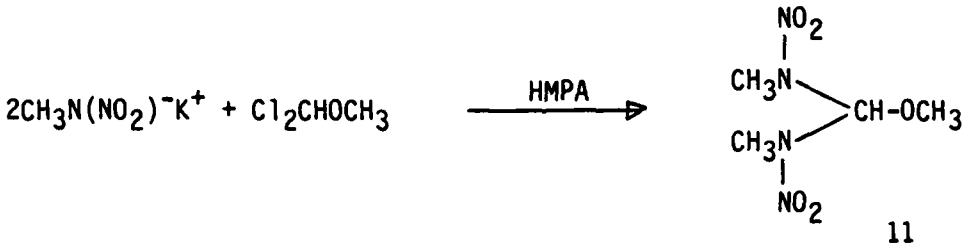
13



10



accomplished by the reaction of potassium methyl nitramine with dichloromethyl methyl ether in low yield. The structure of 11 was confirmed by a crystal

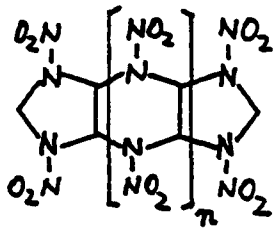


11

17%; MP 53-4°C (dec.)

structure determination (R. Gilardi, NRL), since an isomeric structure analogous to 10 was possible and not distinguishable by spectroscopic or analytical means. 11 is a model structure for 8, and to our knowledge is the first and only known hetero-substituted methylenedinitramine. 11 is not very stable and decomposes slightly above its melting point. As in the case of 10, further reaction with methyl nitramine to 12 was not successful, and 11 is sensitive to both acids and bases. The existence of 11 indicates that

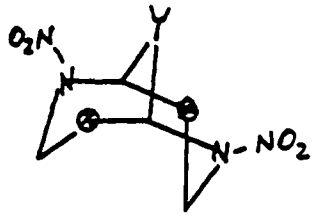
The linear polycyclic compounds (g) and (h) are of interest also.



(g) : 1.95 g/cm^3
(h) : 1.96 g/cm^3

This year's efforts have concentrated on two types of target compounds: (1) Heterobicyclononanes, and (2) linear polycyclic nitramines.

The heterobicyclononanes of interest are structures 6 - 9:



6: Y = N-NO_2; = N-NO_2; ρ_0 (calc'd.) = 1.07 g/cm^3

7: Y = N=NO_2; = $C(NO_2)_2$

8: Y = O; = N-NO_2; ρ_0 (calc'd.) = 1.94 g/cm^3

9: Y = O; = $C(NO_2)_2$

Because structures of this type are not known, the initial effort was to synthesize acyclic analogs in order to assess synthetic approaches and the stability of such compounds.

The reaction of methyl nitramine with ethyl orthoformate gave a mono-substitution product 10, but further reaction to 11 was not possible; 10 is a very reactive substance; all reactions tried led to degradation products. Since the structure of 10 (a liquid) is not fully established, this observation is of limited utility at present. The synthesis of 11 was

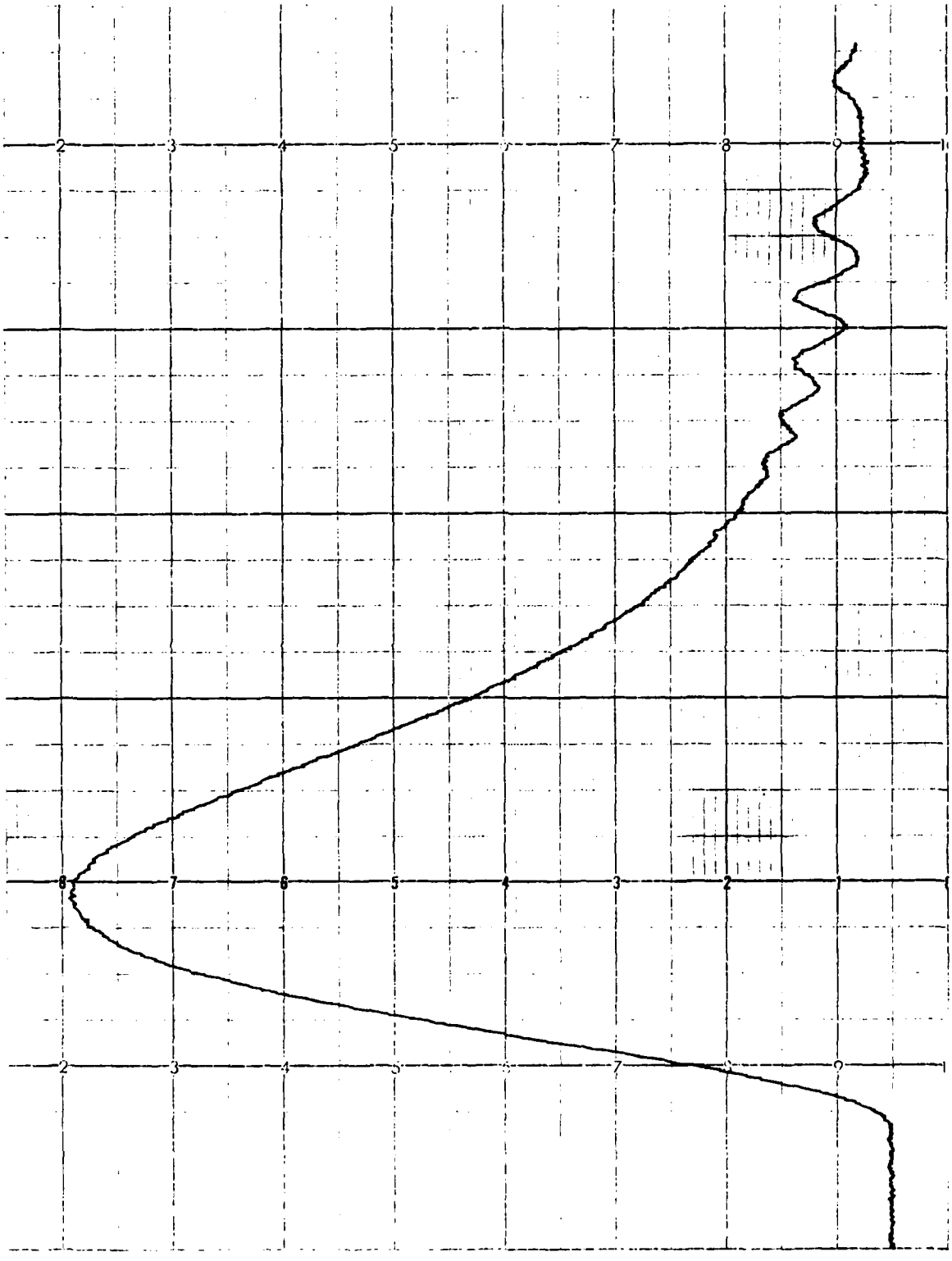


FIGURE 6. GPC OF POLYFORMAL OF $HOCH_2(CF_2)_4CH_2OH$

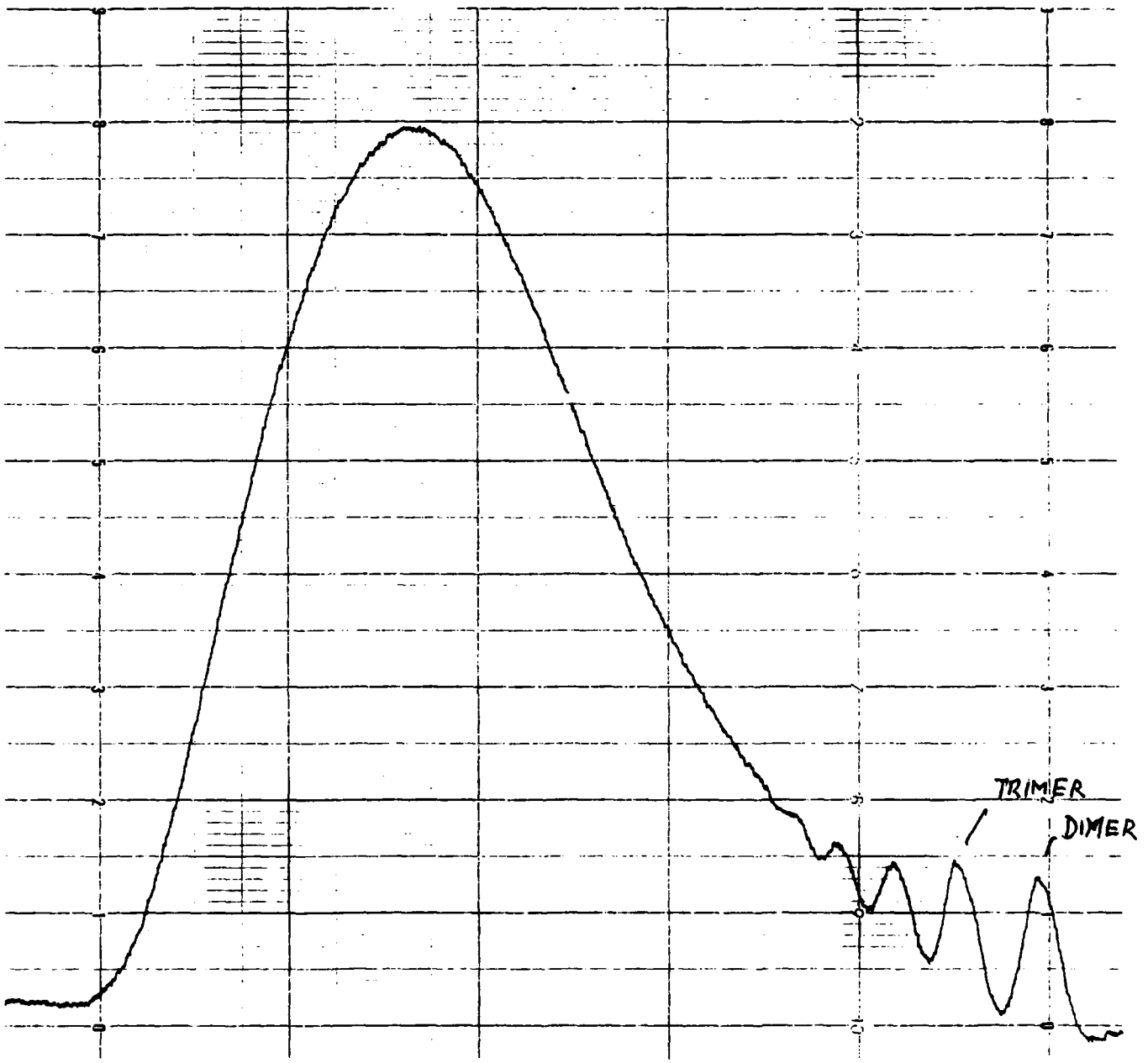


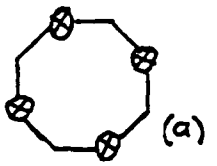
FIGURE 5. GPC OF POLYFORMAL OF $HOCH_2(CF_2)_3CH_2OH$; IMPROVED PROCEDURE

Fig. 5 shows the GPC of a 25g sample of M_n 3100 prepared by this procedure.

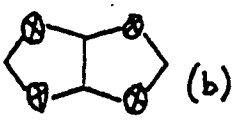
Diol 5 reacted with a slight excess of CH_2O under the same conditions as 4 to give mostly polymer (≈85%) plus a small amount of cyclic formal which was readily removed by heating to 110-120°C in vacuo. The GPC is shown in Fig. 6. Like the polymer from 4, this material is a viscous liquid at room temperature. The molecular weight (M_n) was 6400. Attempts to reduce the molecular weight by reducing the formaldehyde: diol ratio were only moderately successful. When this ratio was reduced from 1.2:1 to 1:1, a M_n of 5300 was obtained. The polymer was shown to be difunctional by hydroxyl analysis and demonstration of curing. Gumstocks of this polymer with FEFO plasticizer are stable only up to a FEFO content of 50 weight percent.

SYNTHESIS OF POTENTIALLY DENSE NITRAMINES

As discussed previously,[5] the calculated densities of cyclic and polycyclic nitramines of the type (b) - (f) are sufficiently higher than that of HMX (a) to make such structures candidates for high energy-density explosives with predicted detonation pressures in the range of 420-470 Kbar. The first set of density values shown below are for the all-nitramines, whereas the numbers in the parentheses are for compounds in which half of the nitraza groups are replaced by gem-dinitro. Note the trend to higher densities with increasing number of rings in the molecule, and the increasing density difference between all-nitramine and mixed nitraza/gem dinitro compounds.

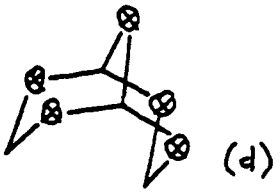


ρo = 1.79 (1.79)

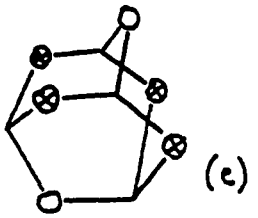


1.91 (1.88)

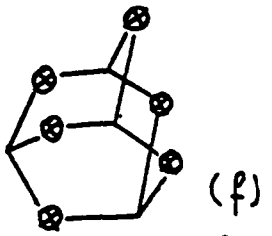
2.05 (1.98) g/cm^3



ρo = 1.97 (1.93)

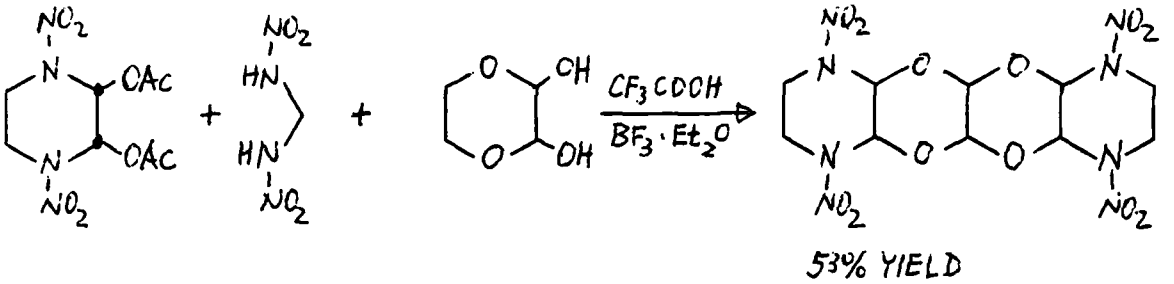


2.08 (2.01)



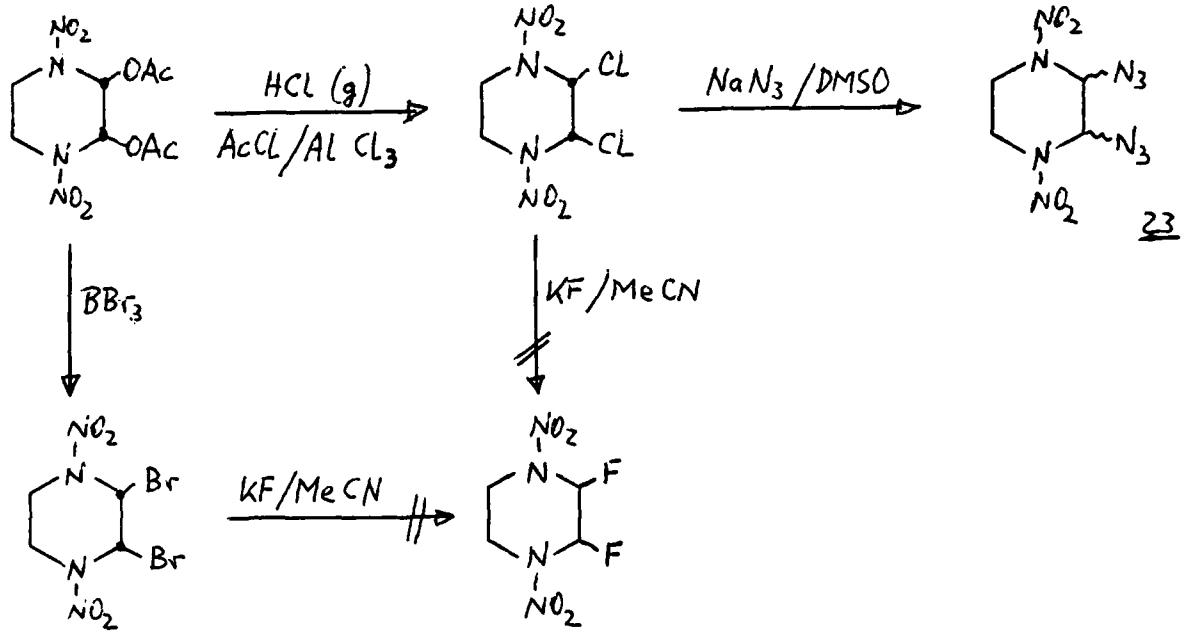
2.11 (2.02) g/cm^3

⊗ = N-NO_2 or alternating N-NO_2/C(NO_2)$_2$



53% YIELD

Although 22a and 22c were readily converted to the corresponding bromide and azide, attempts to obtain the fluoride from either 22c or 22d were not successful, possibly because of an interfering elimination reaction to the olefin (see below).

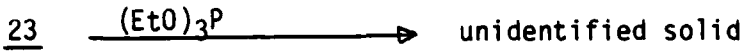


A number of attempts were made to reduce 23 to amines which could participate in condensation reactions to the desired ring systems. Direct hydrogenation gave no identifiable products, but reaction with phosphines gave N_2 evolution

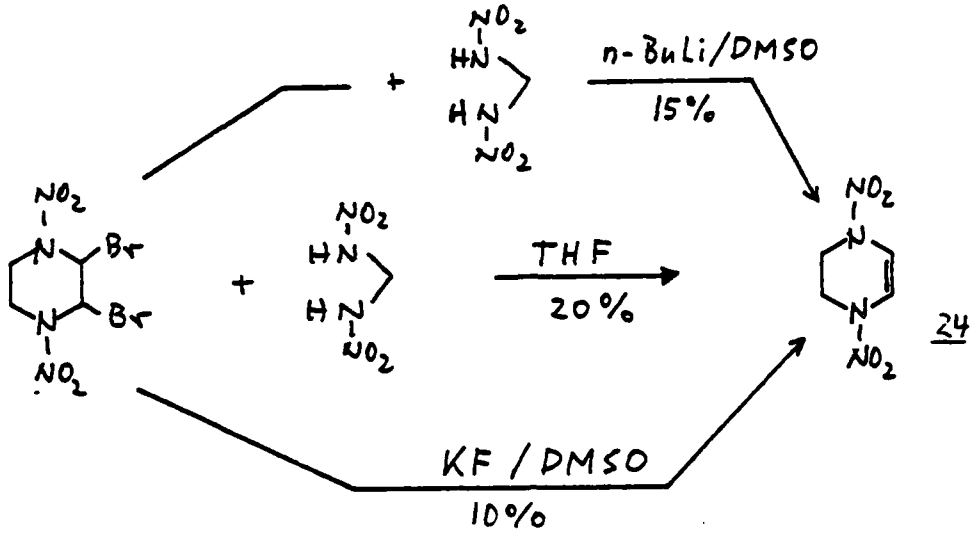
23 $\xrightarrow[18h]{H_2/\text{LINDLAR CAT.}}$ NO REACTION

23 $\xrightarrow{H_2/Ac_2O/Pd\text{-}C}$ yellow oil + polymer

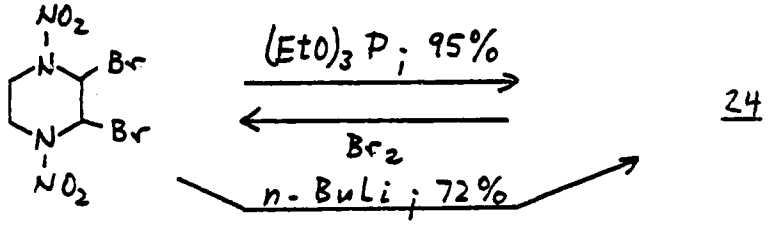
23 $\xrightarrow{Ph_3P}$ unidentified solid



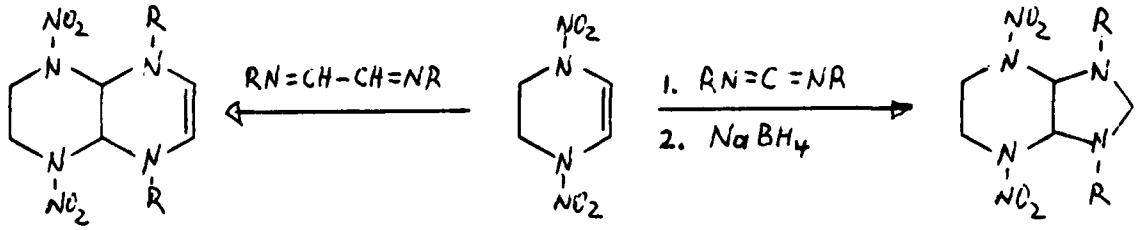
and stable solids, as yet unidentified. These investigations are continuing. An interesting observation was made in reactions of 22d with certain bases or nucleophiles where bromine elimination occured to give the dinitrazaolefin 24.



Better yields of 24 were obtained by treatment of 22d with triethyl phosphite or butyllithium in DMSO:

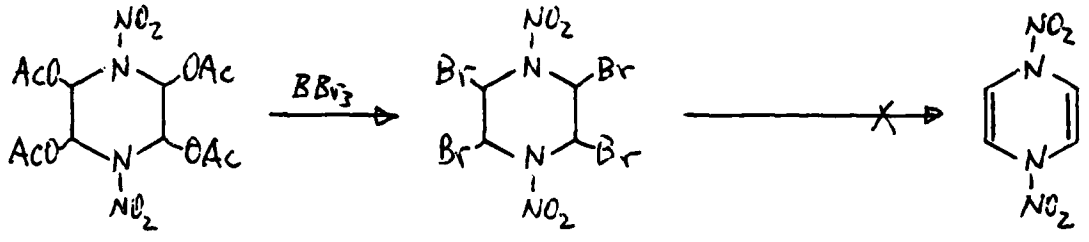


24 is to our knowledge the first reported dinitrazaolefin. It was hoped that it might be an active dienophile for reaction with azadienes which would be a route to the linear polycyclic ring systems discussed above:



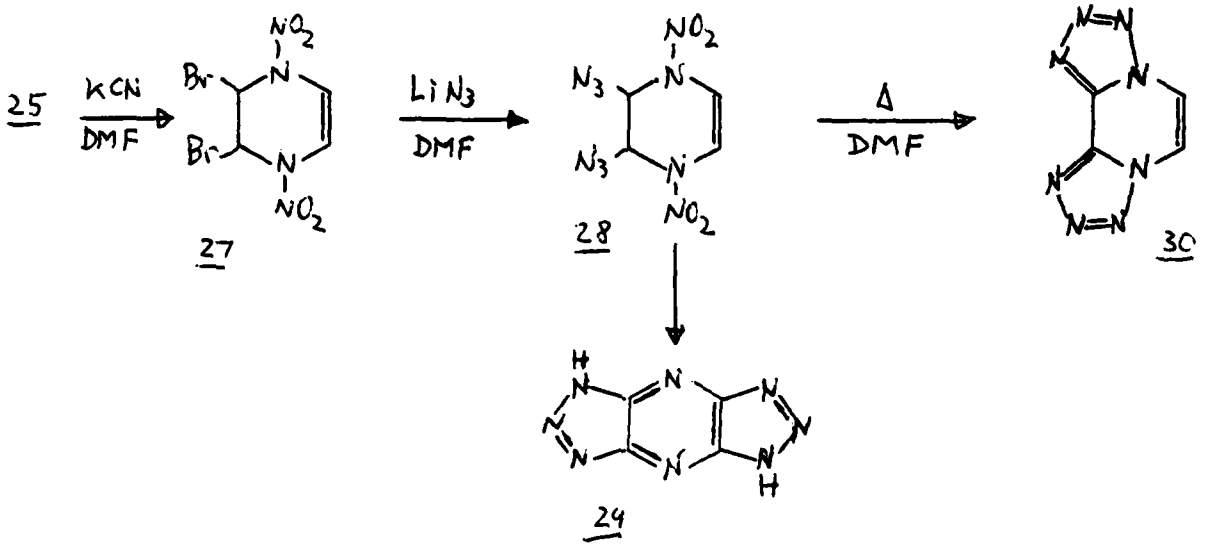
A preliminary investigation of the chemical properties of 24 indicates that the compound polymerizes on heating to about 60° and undergoes little reaction (Diels-Alder) with furan. These investigations are continuing.

Attempts were also made to synthesize the corresponding diene 26. The tetrabromide 25 was prepared from the known tetracetate[7]. A variety of known debrominating reactions were tried but none have been successful so



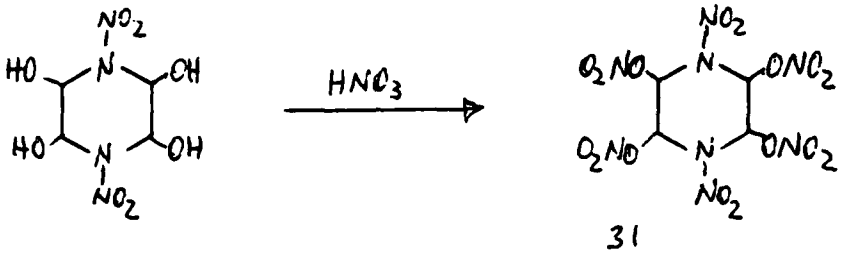
25 26

far due, probably, to the high reactivity or instability of this novel structure. Tetrabromide 25 was, however, converted into two highly reactive compounds 27 and 28. The diazide, 28, loses HNO_2 and cyclizes into a heterocyclic ring system. The structure of this heterocycle, at first thought to be the bistriazolopyrazine 29, has now found by X-ray crystallographic analysis (Gilardi; NRL) to be the bistetrazolopyrazine 30.



25 27 28 30 24

The tetranitratodinitramine 31 was prepared from the tetrahydroxy compound as a possible high-energy oxidizer. Although it crystallized in large colorless prisms, they became opaque within a few hours, and an X-ray density determination could not be carried out successfully. It appears that the physical change in the crystals is not due to surface hydrolysis, but to actual decomposition of the molecule.



31

Experimental Section

Melting points are uncorrected; temperatures are in °C unless noted otherwise. Microanalyses are by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were obtained on a Varian EM-390 spectrometer; chemical shifts are in ppm relative to TMS as internal standard.

Polyformal of 3,3,5,7,7-Pentanitro-5-azanonane-1,7-diol, 1; Modified Procedure.- In a 300 mL 3-neck flask 30g of the diol, 30 mL of dry (molecular sieves) sulfolane, and 2.097g of trioxane were mixed under a nitrogen blanket until homogeneous. 22.5 mL of BF_3 etherate was added with ice-cooling and the mixture was stirred 24 h at room temperature. 200 mL of dichloromethane was added, and the solution was poured into a vigorously stirred mixture of 500 mL of water, 27g of $NaHCO_3$, and 12 mL of 30% H_2O_2. The reaction flask was washed with 50 mL of a 1:1 mixture of dichloromethane and methyl acetate which was combined with the main drowning mixture. After 3.5 h vigorous stirring, the phases were separated and the aqueous phase was washed with 50 mL of 1:1 dichloromethane/methyl acetate. The combined organic layers were freed from solvents on a rotary evaporator (1.5h/40°C). The residue was dissolved in 45 mL of warm methanol and the solution was poured slowly into a vigorously stirred mixture of 270 mL of water and 135 mL of methanol. Stirring was continued until the aqueous phase was only moderately turbid. The liquid phase was poured off and the remaining resin was triturated with water overnight, then dissolved in 300 mL of 1:1 dichloromethane/methyl acetate. The solution was dried ($MgSO_4$) and stripped for 3-4 h/45°C. The residue was triturated with a mixture of 390 mL of dichloromethane and 240 mL of hexane for 72 h, the solvent was decanted and the residue stripped at 45°C for 6 h. Obtained was 25g polymer as a pale yellow powder. GPC analysis (Fig. 1) gave the following data (after exlusion of 8% of low molecular weight cyclic material): M_w = 3780; M_n = 2860; polydispersity = 1,32. The hydroxyl equivalent weight was determined by the NMR method [1] as 1740 ± 0.7%.

Curing of FEFO Solution of Polyformal of 1.- 1.11g of the above polymer was dissolved in 2.0g of FEFO (2,2,2-Fluorodinitroethyl formal) with warming at 50°C, followed by 0.02g each of N-methyl-4-nitroaniline and 2-nitrodiphenylamine. 0.002 mL of dibutyltindilaurate was mixed in thoroughly, followed by 0.091g of PAPI-135. The mixture was degassed at 50°C for 0.5 h and was then cured at 50°C for 4 days to give a clear gumstock with good strength and excellent elongation.

3,3-Dinitropropyl Acetate from Potassium 3,3-Dinitropropanol.- 61.2g of Potassium 3,3-dinitropropanol was dissolved in 190 mL of ice-water. To this was added rapidly with stirring and cooling 18.9 mL of conc. sulfuric acid diluted to 63.1 mL by pouring on ice. After 1 h additional stirring in the melting ice-bath the phases were separated and the aqueous layer was saturated with NaCl and extracted with ether (4x100 mL). The dried ($MgSO_4$) solution was concentrated on a rotary evaporator and the residue was taken up in 65 mL of dichloromethane. 65 mL of acetyl chloride was added with ice-cooling; the mixture was allowed to warm to room temperature and was then refluxed for 2 h. After cooling and drowning on ice, the phases were separated. NaCl was added to the aqueous phase which was extracted with four 100 mL portions of dichloromethane. Usual work-up gave 47.2g of 3,3-dinitropropyl acetate which was pure by ^1H NMR ($CDCl_3$): δ 6.40 (t,1), 4.36 (t,2), 2.58 (overlapping triplets,2), 2.10 (s,3).

Polyformal of 3,5,5-Trinitro-3-azaheptane-1,7-diol,2.- A mixture of 1g of diol 2, 1 mL of dry sulfolane, and 0.1007g of trioxane was stirred until homogeneous. 0.3 mL of BF_3 etherate was added with ice-cooling and the mixture was stirred at ambient temperature for 20 h. 10 mL of Dichloromethane was added and the solution was poured into a mixture of 0.36g of $NaHCO_3$ and 30 mL of water and stirred 3 h with occasional addition of $NaHCO_3$ to adjust the pH to 7. The phases were separated, the dichloromethane layer was dried ($MgSO_4$), filtered, and stripped in vacuo to give the crude polyformal. This material was analyzed by GPC (Fig. 2) without further purification. When larger amounts of BF_3 etherate (0.45 mL, 0.75 mL) were used with an otherwise identical procedure, the products contained larger proportions of low molecular weight cyclic formals.

4,4,6,6-Tetranitro-2,6-diaza-1,7-heptanedicarboxylic Acid.- A solution of 22.8g (0.086 mol) of ethyl 3,5,5-trinitro-3-azapentanoate[8], 185 mL of 50% aqueous methanol, 12.0g (0.086 mol) of ethyl glycine hydrochloride, and 7.2g of formalin (36%, 0.086 mol) was stirred at room temperature while 7.2g (0.086 mol) of $NaHCO_3$ was added in small portions (15 mL additional methanol used to rinse walls of flask after this addition was complete). After 2 h the solution was extracted with dichloromethane and the extract concentrated on a rotary evaporator to an oil. Addition of this oil to a well-stirred and ice-cooled mixture of 51.5 mL of 90% HNO_3 and 51.5 mL of conc. H_2SO_4 was followed by slow heating of the resultant solution to 55-60°C. After 5 min at this temperature the solution was allowed to cool slowly to 20°C and then poured on ice. Extraction with dichloromethane followed by removal of solvent gave the diethyl ester of the title compound as an oil. This was mixed with 85 mL of acetic acid and 17 mL of conc. HCl and heated at 70°C overnight. Volatiles were removed in vacuo, the residue diluted with water, and the diacid extracted with ether. The dried ether solution was concentrated in vacuo and the residue triturated with 100 mL of dichloromethane until it was converted to a powder. The isolated solid (14.3g, 45%) had mp 173°C (dec.); ^{1}H NMR (acetone-d_6) δ 5.43 (s,4), 4.87 (s,4).

Anal. Calcd for $C_7H_{10}N_6O_{12}$: C, 22.71; H, 2.72; N, 22.70. Found: C, 22.48; H, 2.91; N, 22.41.

3,5,5,7-Tetranitro-3,7-diaza-1,9-nonanediol,3.- The above diacid (7.8g, 0.021 mol) was added to an ice-cooled THF.BH_3 solution (1M, 86 mL). After 24 h at 20°C the solution was poured into water and this solution extracted with ether. The dried ether solution was concentrated in vacuo to 8.4g of oil. A dichloromethane/methyl acetate (7:3) solution of the oil was filtered through silia gel and separate fractions were collected. The fractions which crystallized after evaporation of solvent were combined and recrystallized from dichloromethane/acetone to give 5.7g (79%) of diol 3. Material which was dried at 55°C in vacuo overnight and in the presence of P_2O_5 had: mp 95-7°C; ^{1}H NMR (acetone-d_6) δ 5.42 (s,4), 4.06 (m,8).

Anal. Calcd for $C_7H_{14}N_6O_{10}$: C, 24.57; H, 4.12; N, 24.56. Found: C, 24.80; H, 4.01; N. 24.77.

Polyformal of 3,5,5,7-Tetranitro-3,7-diaza-1,9-nonanediol,3.- 1g of Diol 3, 1 mL of dry (sieves) sulfolane, and 0.0789g of trioxane were mixed under a nitrogen blanket until homogeneous. The mixture was cooled in an ice-bath and 0.30 mL of BF_3 etherate was added dropwise with stirring. After 24 h stirring at room temperature, the mixture was diluted with 10 mL of dichloromethane and poured into 30 mL water containing 0.4g of $NaHCO_3$ and 0.4 mL of 30% H_2O_2 which

was stirred. The reaction flask was rinsed with 10 mL of 1:1 dichloromethane/methyl acetate, and the combined drowning mixture was stirred vigorously for about 3 h until the organic solvents had evaporated. The solids were filtered off, washed with water, then triturated with water for 1 h, filtered and dried in air to give 0.95g of a white powder. GPC analysis (Fig. 3) gave the following data (after exclusion of 1.87% of low molecular weight cyclic material): M_w = 2977; M_n = 1943; polydispersity = 1.53.

Curing of FEFO Solution of Polyformal of 3.- 1.57g of polymer and 4.5g of FEFO were mixed by heating to 75°C. At 60°C, 0.0036g of dibutyltin dilaurate were mixed in followed by 0.197g of PAPI-135. The mixture was degassed at 60°C for 0.5 h, then cured 3 days at 60°C and 2 days at 50°C.

Polyformal of 2,2,3,3,4,4-Hexafluoropentane-1,5-diol,4; Direct Method.- A homogeneous mixture of 160.9g of diol and 144.8 mL of 80% sulfuric acid was cooled in an ice-bath while 130 mL of dry dichloromethane and a solution of 27.6g of paraformaldehyde in 100.6 mL of 90% sulfuric acid were added (the latter dropwise). The mixture was stirred vigorously overnight at ambient temperature, then poured onto 1200g of ice (the flask was rinsed with a small amount of ice-water). 1200 mL of ether and 150 mL of 30% hydrogen peroxide were added, and the mixture was stirred vigorously for 1 h. The phases were separated and the ether layer was washed with 1200 mL of 5% KOH solution + 75 mL of 30% hydrogen peroxide, then with 700 mL of 2.5% KOH solution and with 700 mL of water, adding sodium chloride as necessary for phase separation. The ether solution was dried over Drierite with vigorous stirring, filtered through a "fine" sintered glass funnel and stripped in vacuo. Low molecular weight contaminants were removed by heating at 120-130°C/0.1 Torr overnight while the viscous liquid was being stirred slowly. The principal volatile products are unreacted 4 and 5,5,6,6,7,7-hexafluorodioxocane which can be collected in cold traps. The polymer yield was 67.7g; the GPC is shown in Fig. 4. This material had M_n = 4046, M_w = 7584, polydispersity 1.87. The hydroxyl equivalent weight was determined using the NMR method[1] with trifluoroacetic anhydride and was found to be 2098. The sample contained about 5% of cyclic formals which were subtracted from the chromatogram prior to calculation of the molecular weight.

5,5,6,6,7,7-Hexafluoro-1,3-dioxocane.- 100g (0.47 mole) of 2,2,3,3,4,4-Hexafluoropentanediol were added to a solution of 20g (0.67 mole) of trioxane dissoved in dry CH_2Cl_2. While stirring, 40 mL of trifluoromethanesulphonic acid were added at a moderate rate. The reaction mixture was then stirred at room temperature (~20°C) for 90 minutes, after which time 100 mL of water were added with cooling to dilute the trifluoromethanesulphonic acid. The CH_2Cl_2 solution was washed with a dilute basic aqueous hydrogen peroxide solution (3% H_2O_2, 10% KOH) and brine, dried, and filtered. Removal of the CH_2Cl_2 by rotary evaporation yielded a quantitative amount of the crude product as a viscous oil. Distillation gave 88g (83%) of pure 1,3-dioxa-5,5,6,6,7,7-hexafluorocyclooctane, b.p. 165-167°C, m.p. 24-25°C, density 1.584g/cm^3.

Polymerization of 5,5,6,6,7,7-Hexafluoro-1,3-dioxocane.- 2.8g (13.21 mmol) of Hexafluoropentanediol (dried) were dissolved into 34.42g (153.66 mmol) of cyclic formal at 60°C. While stirring, 1.0 mL (11.307 mmol) of triflic acid was added in 100µl increments over the period of 1 h. The stoppered reaction mixture was then allowed to stand at 60° for 24 h, after which time 250 mL dichloroethane were added to dissolve the mass. The solution was washed twice

with 10 mL of 30% H_2O_2 + 115 mL of 10% aqueous NaOH + 125 mL of brine and twice with brine. The dichloroethane solution was then passed through Whatman 1PS filter paper and most of the solvent was removed by rotary evaporation. The residue was subjected to high vacuum at 140° for several hours. Recovered polymer weighed 26.95g (72.5%). GPC analysis gave the following results: M_n = 3100, M_w = 7000, M_w/M_n = 2.14; M_n (calculated) = 2800. Equivalent weight (g of polymer per OH group) was measured by the nuclear magnetic resonance spectrometric technique[1] using trifluoroacetic anhydride to be 1537.

Curing of FEFO Solution of Polyformal of 4.- 0.88g of Polymer and 2.64g of FEFO were mixed at 60°C until homogeneous. 0.001g of Dibutyltin dilaurate was added via a microliter syringe and mixed in, followed by 0.072g of PAPI-135 and again thorough mixing. The mixture was degassed at 50°C for 0.5 h and cured at 50°C for 4 days.

Polyformal of 2,2,3,3,4,4,5,5-Octafluorohexanediol,5.- 3.98 of Diol 5 was dissolved in 2.9 mL 80% sulfuric acid. the solution was stirred and cooled in an ice-bath and 2.6 mL of dichloromethane was added, followed by a solution of 0.456 g of paraformaldehyde in 2 mL of 90% sulfuric acid. After stirring 24 h at room temperature the mixture was poured over 30g of ice, 30 mL of ether and 3.75 mL of 30% H_2O_2 were added, and the mixture was stirred 1 h. The polymer was isolated and purified as described above for the polyformal of 4. Obtained was 3.4g of a resin (81%) which was analyzed by GPC (Fig. 6): M_n = 5400; M_w = 10,700; polydispersity = 1.98.

Curing of FEFO Solution of Polyformal of 5.- The above polymer was miscible with FEFO at 25°C in ratios of 1:1 and 1:1.5. 7.35g of a 1:1.5 polymer-FEFO mixture was mixed with 0.005 mL of dibutyltin dilaurate and 0.157g of PAPI-135. The mixture was degassed at 60° for 0.5 h and was then cured at 60°C for 3 days and at 50°C for 2 days. The gumstock was homogeneous at 50°C but exuded some FEFO after storing at room temperature.

Methyl Diethoxymethylnitramine, 10.- 6.6 mL (40 mmol) of triethylorthoformate and 3.04g (40 mmol) of methylnitramine were mixed with 100 mL of toluene. Toluene was distilled off until the residual volume was 20 mL. The mixture was further concentrated at room temperature on a rotary evaporator and finally at 0.5 Torr. The resulting liquid was distilled at 0.4 Torr and 80°C pot temperature. Three fractions of 1,2, and 1 mL were collected at 56°C. The middle fraction had the best purity but still contained about 15% methylnitramine. All attempts at further purification of this material were unsuccessful. ^{1}H NMR ($CDCl_3$): δ 1.28 (t,6H), 3.23 (s,3H + methylnitramine increment), 3.73 (m,4H), 6.56 (s,1H).

3-Methoxy-2,4-dinitro-2,4-diazapentane,11.- 2.0g (0.0175 mol) of Potassium methylnitramine in 10 mL of hexamethyl phosphoramide (distilled from CaH_2) was cooled in an ice-bath and 0.8 mL (0.00875 mol) dichloromethyl methyl ether was added in 0.1 mL portions at 1 minute intervals. After 15 min. stirring the ice-bath was removed and stirring was continued for 1 h. The mixture was poured into 50 mL of ether and was then washed with 4 x 20 mL of water and with 20 mL of brine. Drying ($MgSO_4$) and stripping gave 0.288g (17.0%) crude product which solidified upon storage at -10°C. The sample was purified by sublimation at 50°C/0.05 Torr; melting point 51.7-53.7°C. ^{1}H NMR ($CDCl_3$): δ 3.33 (s,6H), 3.63 (s,3H), 7.53 (s,1H).

Anal. Calcd for $C_4H_{10}N_4O_5$: C, 24.75; H, 5.19; N, 28.86. Found: C, 24.50; H, 5.14; N, 28.77%.

Reaction of 2,4-Dinitro-2,4-diazapentane (DMMD) with Potassium-t-butoxide.- 0.26g (1.38 mmol) of DMMD was dissolved in 10 mL of ether and 4 mL of tetrahydrofuran and 0.17g (1.38 mmol) of potassium-t-butoxide was added. The mixture was stirred for 3 h. NMR analysis showed that no reaction had occurred. The ether was distilled off and 10 mL of benzene was added. The mixture was refluxed 15 min. during which time dissolution and formation of a precipitate were observed. After cooling, the mixture was filtered through a column of celite and freed of solvent in a rotary evaporator. ^{1}H NMR ($CDCl_3$): δ 3.41 (two s, barely resolved), 3.67 (s), 5.69 (s), 9.02 (2s, barely resolved); the signals at 3.67 and 5.69 ppm are due mainly to DMMD; the signals at 3.41 and 9.02 ppm (ratio ~3:1) may be due to CH_3N=CH- while the missing-$N(NO_2)CH_3$ signal would overlap with the methyl signal of DMMD.

2,3-Dichloro-1,4-dinitropiperazine (22c).- To a stirred solution of 2,3-diacetoxy-1,4-dinitropiperazine (5.84g, 20 mmol) in acetyl chloride (40 mL) at room temperature was added aluminum chloride (3.0g, 22.5 mmol) in 0.5g portions over 45 min. Some of the aluminum chloride coagulated, and was broken-up with a glass rod. After 4 h the mixture was poured into 300 mL of ice and water and filtered to yield 4.25g (86.7%) of white solid: MP 143-146°C.

Similarly, 2,3-diazido-1,4-dinitropiperazine reacted with aluminum chloride in acetylchloride, with gas evolution (N_2) to give the dichloride in 78% yield.

2,3-Dibromo-1,4-dinitropiperazine (22d).- To a stirred solution of 2,3-diacetoxy-1,4-dinitropiperazine (2.92g, 10 mmol) in CH_2Cl_2(50 mL), cooled in ice, was added boron tribromide (20 mL of 1.0M in CH_2Cl_2). The ice bath was removed and stirring was continued for 1 h. The mixture was then diluted with CH_2Cl_2 (50 mL), washed with water (2 x 25 mL), 5% $NaHCO_3$ (2 x 30 mL), dried ($MgSO_4$), and evaporated to give a white solid. Trituration with hexane, and filtering yielded 3.03g (90.7%): MP 130-131°C (dec). The analytical sample, of same MP was recrystallized from benzene-isopropyl ether. ^{1}H NMR (CD_2Cl_2): δ 3.77 and 4.70 (d, 4H, CH_2, J = 10Hz), 7.20 (s, 2H, CH) ppm; mass spectrum (CI, CH_4) m/z 83 (100), 253 (60), 255 (M+1-HBr, Br = 81, 58) 333 (6), 335 (12) 337 (M+1, Br = 81, 5), 365 (M+29, 1.4)

Anal. Calcd for $C_4H_6Br_2N_4O_4$: C, 14.39; H, 1.81; N, 16.78; Br, 47.86. Found: C, 14.40; H, 1.72; N, 16.76; Br, 47.51.

2,3-Diazido-1,4-dinitropiperazine (23).- A solution of 2,3-dichloro-1,4-dinitropiperazine (2.45g, 10 mmol) and sodium azide (2.60g, 40 mmol) in dimethyl sulfoxide (60 mL) was stirred at room temperature for 24 h. The mixture was then poured into ice and water (250 mL) and the solid filtered to yield 1.56g (60.5%) of white solid: MP 107-110°C. Recrystallization from benzene-hexane gave colorless, flat needles: MP 110-112°C; IR (KBr) 2150 (sh)cm^{-1}, and 2120, 1570, 1290; ^{1}H NMR (CD_2Cl_2): δ 3.89 and 4.50 (d, 4H, CH_2, J = 9Hz), 6.50 (s, 2H, CH) ppm.

Anal. Calcd for $C_4H_6N_{10}O_4$: C, 18.61; H, 2.34; N, 54.26. Found: C, 18.86; H, 2.37; N, 54.32.

1,4,6,9-Tetranitro,1,4,6,9-tetraaza-5,10-dioxaperhydroanthracene and 1,4,7,10-tetranitro-1,4,7,10-tetraaza-5,6,11,12-tetraoxaperhydronapthacene.- A mixture of 2,3-diacetoxy-1,4-dinitropiperazine (5.84g, 20 mmol), methylenedinitramine (2.72g, 20 mmol) and trifluoroacetic acid (200 mL) was heated to 60°C to dissolve the solids and then cooled to room temperature. Boron trifluoride etherate (3 mL, 3.46g, 24.4 mmol) was added and the mixture stirred for 18 h. The precipitate was filtered to give the perhydroanthracene (2.95g, 77.4%) as a white solid: MP 289°C (rapid dec). The solid was dissolved in hot DMF (100 mL) and diluted with ethanol (100 mL). Cooling and filtering gave the pure product: MP 292°C (dec); ^{1}H NMR (Me_2SO-d_6): δ 4.35 (m, 8H, CH_2), 6.49 (s, 4H, CH); mass spectrum (CI, CH_4) m/z 99 (100), 197 (30), 381 (M+1, 0.7), 410 (M+NO, 1.1), 421 (M+41, 0.33).

Anal. Calcd for $C_8H_{12}N_8O_{10}$: C, 25.27; H, 3.18; N, 29.47. Found: C, 25.40; H, 3.26; N, 29.30.

The DMF-ethanol filtrate from the above recrystallization was diluted with isopropyl ether (200 mL) and cooled in a refrigerator overnight to deposit 90mg of white solid. This product, upon heating in a capillary MP tube did not exhibit the rapid decomposition noted above for the perhydroanthracene, but slowly carbonized above 300°C. Spectroscopic and elemental analysis showed this to be the perhydronapthacene. ^{1}H NMR showed a pair of multiplets centered at δ 3.96 and 4.43 (8H, CH_2), 5.64 (s, 2H, OCHO), 6.75 (s, 4H, NCHO); mass spectrum (CI, CH_4) m/z 99 (100), 439 (M+1, 1.2) 467 (M+29, 1.2), 479 (M+41, 0.25).

Anal. Calcd for $C_{10}H_{14}N_8O_{12}$: C, 27.40; H, 3.22; N, 25.57. Found: C, 27.42; H, 3.19; N, 25.62

1,4,7,10-Tetranitro-1,4,7,10-tetraaza-5,6,11,12-tetraoxaperhydronapthacene.- A mixture of 2,3-diacetoxy-1,4-dinitropiperazine (2.92g, 10 mmol), methylenedinitramine (1.36g, 10 mmol), p-dioxane-2,3-diol (1.20g, 10 mmol), and boron trifluoride etherate (3 mL, 3.46g, 22.4 mmol) in trifluoroacetic acid was stirred at room temperature for 18 h. The precipitate was filtered to give 1.17g (53.4%) of white solid: MP darkens at ~270°C and carbonizes above 300°C. The ^{1}H NMR spectrum showed only traces of the perhydroanthracene. Recrystallization from DMF-ethanol gave 863mg (39.4%) of the perhydronapthacene: MP - carbonizes above 300°C. The NMR spectrum of this product indicated that it was stereochemically more complex than the product isolated above.

2,3-Dehydro-1,4-dinitropiperazine (24).-

(a) From 2,3-dibromo-1,4-dinitropiperazine and triethyl phosphite. A mixture of the dibromide (2.67g, 8 mmol) and triethylphosphite (10 mL) was stirred at room temperature for 18 h. Hexane (10 mL) was added and the solid was filtered to yield 1.32g (95%) of yellow solid: MP 127°C (dec); ^{1}H NMR (Me_2CO-d_6): δ 4.59 (s, 4H, CH_2), 7.19 (s, 2H, CH); mass spectrum (CI, CH_4) m/z 83 (100), 128 (52), 175 (M+1, 2.4). The product reacted with bromine in CH_2Cl_2 to regenerate the dibromide in 65% yield.

Anal. Calcd for $C_4H_6N_4O_4$: C, 27.59; H, 3.47; N, 32.18. Found: C, 27.59; H, 3.49; N, 31.93.

(b) From the dibromide and methylsulfinylcarbanion.- A stirred mixture of DMSO (15 mL) and THF (5 mL) was cooled to 0°C and n-butyllithium (4.58 mL of 2.4M in hexane, 11 mmol) was added. The dibromide (1.67g, 5 mmol) in THF (5 mL) was then added dropwise over 5 min. The dark solution was stirred at room

temperature for 45 min, then poured into a mixture of ice and water (70 mL). Filtering gave 630mg (72.3%) of tan solid: MP 123°C (dec). The solid was dissolved in CH_2Cl_2 and filtered through a short column of silica gel. Evaporation of the solvent gave yellow crystals: MP 127°C (dec).

(c) From the dibromide and potassium cyanide.- A stirred solution of the dibromide (1.0g, 3 mmol) in DMF was cooled to 0°C and potassium cyanide (651mg, 10 mmol) was added. The solution was warmed to room temperature over 30 min and the DMF was then evaporated under reduced pressure at 50°C. The red residue was diluted with water (15 mL), cooled in ice and then filtered to give 450mg (86.2%) of yellow solid: MP 126°C (dec).

(d) From the dibromide and lithium azide.- A stirred solution of the dibromide (2.0g, 6 mmol) in DMF (10 mL) was cooled to 0°C and a solution of lithium azide (979mg, 20 mmol) in DMF (15 mL) was added over 15 min. The reaction mixture becomes orange and nitrogen is evolved. After warming to room temperature over 1 h, the DMF was evaporated under reduced pressure at 50°C and the residue was diluted with water (30 mL). Cooling this in ice and then filtering gave 823mg of pale yellow solid: MP 105-106°C (dec). The ^1H NMR spectrum (Me_2CO-d_6) showed that this product contained about 16% of 2,3-diazido-1,4-dinitropiperazine in addition to the unsaturated dinitramine.

2,3,5,6-Tetraacetoxy-1,4-dinitropiperazine and 2,5-diacetoxy-3,6-dinitrato-1,4-dinitropiperazine.- Anhydrous nitric acid (40 mL) was added dropwise to a stirred suspension of disodium 2,3,5,6-tetrahydroxy-1,4-disulfuric acid (20g, 54.6 mmol) in acetic anhydride (60 mL) over 15 min, while the temperature was maintained at ~30°C. The temperature was kept at 30°C for an additional 30 min by occassional cooling with a cold water bath. Stirring was continued for 2 h longer as the temperature slowly dropped to room temperature. The mixture was then poured into a mixture of ice and water (300 mL) and the resulting white paste was washed several times with cold water by decantation. The paste was squeezed with a flat spatula to remove most of the water and then dissolved in a mixture of acetic anhydride and acetic acid (v:v, 1:1, 200 mL). Sulfuric acid (2 drops) was then added and the solution was heated slowly in an oil bath. A vigorous evolution of nitrogen oxides occurs between 40-70°C (decomposition of some acetyl nitrate), and the temperature was then raised to reflux for 4 h. The nearly colorless solution was evaporated under vacuum at 50°C and the residue triturated with ether (40 mL) and filtered to give 9.25g (39.6%) of the crude tetraacetate as a white solid: MP 255-260°C. Recrystallization from ethanol gave the pure material: MP 266-268°C.

The ether filtrate was cooled in a refrigerator for several days to deposit 2.30g (9.9%) of the diacetoxy dinitrato product: MP 157-161°C. Recrystallization from CH_3CN-isopropyl ether gave white crystals: MP 169-170°C.

2,3,4,6-Tetrabromo-1,4-dinitropiperazine (25).- A solution of 2,3,4,6-tetraacetoxy-1,4-dinitropiperazine (4.08g, 10 mmol) in CH_2Cl_2 (100 mL) was cooled to 0°C and boron tribromide (40 mL of 1.0M in CH_2Cl_2) was added. The solution was stirred at 0°C for 5 min and then warmed to room temperature during 1 h. The mixture was diluted with CH_2Cl_2 (100 mL) and washed with water, 5% aqueous $NaHCO_3$, saturated salt solution, dried ($MgSO_4$) and evaporated to leave a white solid. Trituration with isopropyl ether and filtering gave 4.50g (91.5%) of product: MP 147-148°C (dec). Recrystallization from benzene gave colorless prisms: MP 154-155°C (dec); ^1H

NMR (CD_2Cl_2): δ 7.34 (s, 4H, CH); mass spectrum (CI, CH_4) m/z 81 (100), 409 (4), 411 (9.8), 413 (9.3), 415 (M+1-HBr, Br = 81, 3.7), 525 (M+29, Br = 81, 0.14).

Anal. Calcd for $C_4H_4Br_4N_4O_4$: C, 9.77; H, 0.82; N, 11.39; Br, 65.00. Found: C, 9.80; H, 0.78; N, 11.28; Br, 64.75.

Similarly, 2,5-diacetoxy-3,6-dinatrato-1,4-dinitropiperazine was brominated with BBr_3 to the tetrabromopiperazine in 95% yield.

Bis-tetrazolodehydropiperazine (30).- A stirred solution of lithium azide (2.94g, 60 mmol) in DMF (35 mL) was cooled to 0°C during the dropwise addition of 2,3,5,6-tetrabromo-1,4-dinitropiperazine (2.95g, 6 mmol) in DMF (25 mL) over 15 min. The mixture was stirred at 0°C for 5 min longer and then warmed to room temperature during 1 h. The DMF was evaporated under reduced pressure at 50°C and the residue was diluted with ice-cold water (25 mL). The mixture was cooled in an ice bath for 10 min longer and then filtered to give 450mg (46.2%) of yellow solid: MP 259°C (violent dec). Recrystallization from methyl isobutyl ketone gave yellow prisms: MP 264°C (violent dec) - darkening above 200°C. ^1H NMR (Me_2CO-d_6): δ 9.32 (s, 2H); mass spectrum (CI, CH_4) m/z 43 (100), 163 (M+1, 44).

Anal. Calcd for $C_4H_2N_8$: C, 29.63; H, 1.24; N, 69.12. Found: C, 29.60; H, 1.14; N, 69.46.

2,3-Dibromo-5,6-dehydro-1,4-dinitropiperazine (27).-

(a) From 2,3,5,6-tetrabromo-1,4-dinitropiperazine and potassium cyanide. A stirred solution of the tetrabromide (984mg, 2 mmol) in DMF (25 mL) was cooled to 0°C and potassium cyanide (1.30g, 20 mmol) was added all at once. Stirring was continued at 0°C for 5 min, and the mixture was then warmed to room temperature over 30 min. The DMF was evaporated under vacuum at 50°C, and the dark red residue was diluted with ice-cold water (20 mL) and cooled in an ice bath for 15 min. The precipitate was filtered, washed with water, and dried to give 335mg (50.4%) of almost white solid: MP 82°C (dec); ^1H NMR (Me_2CO-d_6): δ 7.47 (s, 2H, CH), 7.73 (s, 2H, CHBr); mass spectrum (CI, CH_4) m/z 81 (100), 284 (.4), 286 (17.7), 288 (M+1-HNO_2, Br = 81, 8.8), 331 (0.4), 333 (0.74), 335 (M+1, Br = 81, 0.3).

The dibromoolefin slowly decomposed upon standing at room temperature for several days. It could be stored in a refrigerator at 0°C for over a month without appreciable decomposition. In solution (acetone, CH_2Cl_2) it decomposed completely within 2 h.

(b) From the tetrabromide and potassium fluoride.- To a stirred solution of the tetrabromide (492mg, 1.0 mmol) in DMSO (3 mL) was added potassium fluoride (581mg, 10 mmol) all at once. After 45 min the mixture was diluted with cold water (15 mL), cooled in ice for 15 min, and then filtered to give 114mg (34.3%) of white solid: MP 83°C (dec).

2,3-Diazido-5,6-dehydro-1,4-dinitropiperazine (28).- A stirred solution of 2,3-dibromo-5,6-dehydro-1,4-dinitropiperazine (996mg, 3 mmol) in DMF (25 mL) was cooled to 0°C and lithium azide (1.47g, 30 mmol) was added all at once. The mixture was warmed to room temperature during 1 h and the DMF was then evaporated under vacuum at 35°C. The residue was diluted with cold water (30 mL), cooled in ice for 10 min, and filtered to give 210mg of white solid. NMR analysis showed that this was a mixture of the diazide and the bis-tetrazolodehydropiperazine in about equal amounts. The solid was dissolved in CH_2Cl_2 and filtered through a small column of silica gel. Evaporation of the

solvent gave the pure diazide: MP 95°C (violent dec); IR (KBr) 2160 (sh) and 2120 cm^{-1} (N_3), 1550, 1265 cm^{-1} (NO_2); ^1H NMR (Me_2CO-d_6) δ 7.17 (s, 2H), 7.27 (s, 2H); mass spectrum (CI, CH_4) m/z 44 (100), 94 (29), 165 (25), 185 (14), 210 (22), 214 (M+1-HN_3, 32), 257 (M+1, 0.64).

Anal. Calcd for $C_4H_4N_{10}O_4$: C, 18.75; H, 1.57; N, 54.69. Found: C, 18.40; H, 1.58; N, 55.01.

2,3,5,6-Tetranitrato-1,4-dinitropiperazine (31).- Anhydrous nitric acid (7 mL) was stirred and cooled to 0°C during the addition of trifluoroacetic anhydride (10 mL) over 5 min. After 10 min, disodium-2,3-5,6-tetrahydroxy-1,4-disulfuric acid (2.48g, 7 mmol) was added in portions over 5 min. The mixture was stirred at 0°C for 1 h and then at room temperature for 18 h. Volatiles were then removed under reduced pressure and the residue was diluted with ice-cold water (30 mL) and the mixture extracted with CH_2Cl_2. The extracts were washed with 5% aqueous $NaHCO_3$, saturated salt solution, dried ($MgSO_4$), and evaporated to leave a solid. Trituration of this with isopropyl ether and filtering gave 535mg (18.2%) of white solid: MP 144-145°C (dec). Recrystallization from benzene gave colorless prisms of the same MP: ^1H NMR (Me_2CO-d_6): δ 8.33 (s, 4H, CH); mass spectrum (CI, CH_4) m/z 46 (100), 47 (32), 48 (65), 358 (M+1-HNO_3, 0.6).

Upon standing in a closed container for 24 h, the colorless prisms became cloudy and opaque. After several days, red fumes of NO_2 were observed in the container. A satisfactory elemental analysis could not be obtained.

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